ISTANBUL TECHNICAL UNIVERSITY ★ GRADUATE SCHOOL OF SCIENCE ENGINEERING AND TECHNOLOGY

SYNTHESIS OF PHOTOCHROMIC COATING MATERIALS

M.Sc. THESIS

Mehtap DELİBAŞ

Department of Polymer Science and Technology

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İSTANBUL TEKNİK ÜNİVERSİTESİ ★ FEN BİLİMLERİ ENSTİTÜSÜ

FOTOKROMİK KAPLAMA MALZEMELERİNİN SENTEZİ

YÜKSEK LİSANS TEZİ

Mehtap DELİBAŞ
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Polimer Bilimi ve Teknolojisi Anabilim Dalı

Polimer Bilimi ve Teknolojisi Programı

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HAZİRAN 2013

Mehtap DELİBAŞ, a **M.Sc.** student of ITU **Institute of Science and Technology** student ID 515111018, successfully defended the **thesis/dissertation** entitled "**SYNHESIS OF PHOTOCHROMIC COATING MATERIALS**", which she prepared after fulfilling the requirements specified in the associated legislations, before the jury whose signatures are below.

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Date of Submission : 3 May 2013
Date of Defense : 5 June 2013

To my mother and Ceren,

FOREWORD

This master study has been carried out in POLMAG Laboratory (Polymeric Materials Research Group), located at Faculty of Science and Letters in Istanbul Technical University.
I would like to thank my advisor, Prof. Dr. İ. Ersin SERHATLI, for sharing generously his knowledge and experience with me, for his guidance, inspiration, encouragament throughout this study, and for his opportunity to work in his research group.
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JUNE 2013

Mehtap DELİBAŞ
Textile Engineer

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ABBREVIATIONS

DBDTL	**:** Dibutyltindilaurate
DPGDA	**:** Dipropyleneglycoldiacrylate
F	**:** Phthalocyanine
HDDA	**:** 1,6-hexandioldiacrylate
PMDETA	**:** N,N,N′,N″,N″-Pentamethyldiethylenetriamine
PMMA	**:** Poly(methyl methacrylate)
SP	**:** Spiropyran
SP-PMMA	**:** Spiropyran end functionalized triphenyl phospine oxide PMMA
SP-UA	**:** Spiropyran linked urethane acrylate
SO	**:** Spirooxazine
VSP	**:** Vinylated spiropyran

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SYNTHESIS OF PHOTOCHROMOC COATING MATERIALS

SUMMARY

Photochromism is a reversible colour change between two states having separate absorption spectra. If a photochromic material is exposed with ultraviolet irradiation, it will change the colour. Photochromism is based on some mechanism like ring opening-ring closing and cis-trans isomeration.

Photochromic materials have some industrial applications like opthalmic lenses, nail-polish and t-shirt.

Photochromic materials can be physically dispersed in polymeric systems or chemically bonded to a polymer.

For spiropyran having functional group, indoline and alkyl halides are used to synthesize indolium salt, then indolium salt is coupled with salicaldehyde.

Urethane acrylate coatings have some properties like toughness, flexibility, adhesion and non-yellowing they are important for textile applications. Urethane acrylate is used in floor, paper, plastic, and textile coating.

Flame retardance polymers are significant for textile applications. Phosphorus compounds as flame retardant in polymers are well known. Flame retardant materials can be incorporated into polymers by chemically bonding or physically blending.

Ultraviolet curing (UV curing) is a photochemical process in which high-intensity ultraviolet light is used to instantly cure or dry inks, coatings or adhesives. Offering many advantages over traditional drying methods, UV curing has been shown to increase production speed, reduce reject rates, improve scratch and solvent resistance, and facilitate superior bonding.

In this thesis, photochromic coating materials were synthesized.

Hydroxy functional spiropyran, vinylated spiropyran and spiropyran linked urethane acrylate were synthesized. Synthesized spiropyran based photochromic compounds and commercial spirooxazine were used for urethane acrylate coating formulations.

Also phthalocyanine was used in these formulations to analyse its effect on decolouration of urethane acrylate coatings. To characterize coating materials UV absorbance, water contact angle, pencil hardness and tensile properties were determined.

Triphenyl phosphine oxide containing poly(methyl methacrylate) was used as bifunctional macroinitiator and spiropyran end functionalized polymer was synthesized via atom transfer radical polymerization (ATRP). Polymer was characterized by ultraviolet-visible (UV) spectroscopy, ^{1}H nuclear magnetic resonance (NMR) spectroscopy, and gel permeation chromatography.

FOTOKROMİK KAPLAMA MALZEMELERİNİN SENTEZİ

ÖZET

Fotokromizm, bir kimyasal yapının iki farklı absorbsiyon spektrası arasında tersinir olarak renk değiştirmesidir. Eğer fotokromik bir malzeme ultraviyole ışınlarına maruz bırakılırsa rengi değişir. Fotokromizm halka açılması-halka kapanması ve cis trans izomerizasyonu gibi mekanizmalara dayanır.

T tipi fotokromizm, fotokromik malzemenin renkli halinden renksiz haline dönüşünün ısı veya görünür ışık yoluyla dönmesidir. P tipi fotokromizm, fotokromik malzemenin renkli halinden renksiz haline dönüşünün fotokimyasal olarak dönmesidir.

Eğer bir fotokromik malzeme karanlıkta renksiz formunda ve UV altında renkli hale geçiyorsa, pozitif fotokromizm olarak adlandırılır. Negatif fotokromizm, fotokromik malzemenin karanlıkta renkli ve UV ışını ile renksiz hale geçtiği fotokromizm tipidir.

Fotokromik malzemeler, gözlük camlarında gözü UV ışınlarından korumak için kullanılır. Ojelerde ve tişörtlerde de kullanım alanı bulmaktadır. Baskı malzemeleri, bilgi depolama, sinyal iletim sistemi, moleküler anahtarlar, sensörler, kozmetik gibi potansiyel uygulamalara sahiptirler. Fotokromik malzemeler bir polimer sisteminin içine fiziksel karıştırma yöntemiyle eklenebilir veya polimer yapısına kimyasal olarak bağlanabilirler.

Bu çalışmada, fotokromik kaplama malzemeleri sentezlenmiştir. Hidroksi fonksiyonel spiropiran, vinil grubu içeren spiropiran ve spiropiran bağlanmış üretan akrilat sentezlenmiştir. Sentezlenen spiropiran bazlı fotokromik yapılar ve ticari spirooksazin üretan akrilat kaplama formülasyonları için kullanılmıştır. Trifenil fosfin oksit içeren poli(metil metakrilat) iki fonksiyonlu bir başlatıcı olarak kullanılmış ve uçlarında spiropiran bulunan bir polimer ATRP ile sentezlenmiştir.

Genel olarak akrilik monomer içeren fotokromik maddeler UV ile çapraz bağlanarak fotokromik kaplama filmi oluştururlar. UV ışınlarıyla kürleştirme, yüksek yoğunlukta ultraviyole ışık kullanarak hızlı bir şekilde kürlenme veya boyaların, kaplamaların kurumasını sağlayan kimyasal bir prosestir. Geleneksel kurutma yöntemlerine göre, üretim hızını arttırmak, çizilme ve çözücü dayanımını iyileştirmek, bağ oluşmasını kolaylaştımak gibi avantajları vardır.

Spirobenzopiranlar fotokromik özellik gösteren ve ilgili çok çalışma yapılmış kimyasal bir yapıdır. Renksiz spiropiranın UV ile uyarılması karbon-oksijen bağının heterolitik bölünmesine neden olur ve halka açılarak renkli merosiyanin formuna geçer. Spirooksazinler, azot içeren spiropiran benzeri yapılardır ve fotobozunmaya

karşı oldukça dirençlidirler. Fotobozunmaya karşı olan bu direnç yorulma direnci olarak bilinir. Güneş gözlüğü gibi güneşten korunmak için tasarlanan ürünlerde önemli bir özelliktir.

Uyaranlara duyarlı polimerler, akıllı malzemelerin ve cihazların geliştirilmesi için yoğun olarak araştırılmıştır. Çalışmaların bazıları ölçülebilir bir tepki almak için polimer matrisine dahil edilecek minimum spiropiran miktarını belirlemektir. Bu aynı zamanda spiropiranın polimer içindeki konumlanmasıyla da alakalıdır.

Fonksiyonel gruba sahip spiropiran sentezlemek için, indolin ve alkil halidler kullanılarak tuz yapısı oluşturulur, daha sonra aldehit kullanılarak bu iki yapı bağlanır ve spiropiran sentezlenmiş olur. Hidroksi fonksiyonel spiropiran sentezlemek için 2,3,3-trimethylindolenine ve 2-bromoethanol kullanılarak tuz yapısı elde edilmiştir. Daha sonra bu tuz aldehitle reaksiyona sokularak sentez tamamlanmıştır.

Vinil grubu içeren spiropiran sentezlemek için hidroksi fonksiyonel spiropirana trietilamin katalizörü varlığında akriloil klorürle vinil grubu bağlanmıştır.

Üretan akrilat kaplamalar tokluk, esneklik, yapışma ve sararmama gibi tekstil uygulamaları için de önemli olan özelliklere sahiptir. Üretan akrilatlar yer, kağıt, plastik ve tekstil kaplamalarında kullanılırlar. Spiropiran bağlanmış üretan akrilat sentezlemek için izosiyanat içeren üretan akrilat yapısına hidroksi fonksiyonel spiropiran bağlanmıştır.

Spiropiranların açık formdaki renkli halinden kapalı formdaki renksiz haline dönüşleri yavaş gerçekleşmektedir. Halka açılma-kapanma mekanizmasını hızlandırmak için metal iyonları kullanılmaktadır, ftalosiyaninlerde bu amaçla kullanılabilecek malzemelerdir. Ftalosiyaninler yarı iletken maddelerdir, bu özelliği dolayısıyla fotokromik kaplamalaırn renklerinin geri dönüşünü hızlandıracağı düşünülmüştür. Daha önce bu yönde yapılmış çalışmalar olup olumlu sonuçlar alınmıştır. Ftalosiyanin de üretan akrilat kaplamaların renginin geri dönüşündeki etkisini anlamak için üretan akrilat kaplama formülasyonlarda kullanılmıştır.

Kaplama malzemeleri günlük hayatta hemen hemen her yerde bulunurlar (duvar kaplamaları, otomobil boyaları gibi). Dekoratif görünüm veya koruma amaçlı olarak kullanılırlar. Bir kaplama istenen görünümü (renk, parlaklık) sağlama, gerekliyse korozyona, çiziğe, aşınmaya ve kimyasal ataklara(mobilya kaplamaları üzerinde, kırmızı şarap ve kahve gibi) karşı koruma ya da otomotiv kaplamaları için ağaç rezini ve kuş pisliğinin etkisine karşı koruma bir kaplamanın sağlaması gereken temel fonksiyonlarıdır.

Bu çalışmada kaplama malzemeleri, belirtilen fotokromik etken maddelerin, üretan akrilat reçinesi, kullanılan iki farklı akrilik monomer ve foto başlatıcı ile hazırlanan karışımlara ilave edilerek hazırlanmıştır. Bir grup filmde ftalosiyanin eklenerek hazırlanmıştır. Filmler içerdikleri fotokromik yapı ve ftalosiyanin içeren içermeyen olarak karşılaştırılmıştır. Hazırlanan formülasyonlar cam yüzeylere aplikatör ile kaplanmış ve konveyörden geçirilerek UV ile kürleştirme yapılmıştır.
Kaplama malzemelerini karakterize etmek için UV absorbans, su temas açısı, ve mekanik özellikleri incelenmiştir. UV spektroskopisi ile kürlenen filmlerin UV

absorbansları alınmış ve filmler etken maddelerine göre ayrılarak ftalosiyanin içeren ve içermeyen olarak karşılaştırılıp, ftalosiyaninin fotokromik kaplamada rengin dönüşüne olan etkisine bakılmıştır. Spiropiran ve spirooksazin kapalı formda hidrofobik özellik gösterirler. UV ışınıyla halka açıldığında hidrofilik özellik gösterirler. Yüzeylerin bu özellikleri su temas açısı testi ile tespit edilir. UV ile kürlenen filmlerin su temas açılarına bakılarak fotokromik yapıların açık ve kapalı formları hakkında bilgi edinilmiştir. Filmler geri dönüş hızları açısından karşılaştırılmıştır.

Yanma geciktirici polimerler tekstil uygulamarında önemlidir. Fosfor bileşikleri, polimer uygulamarında en iyi bilinenlendendir. Yanma geciktirici maddeler polimerlerle fiziksel olarak karıştırılabilir veya polimerlere kimyasal olrak bağlanabilirler. Yeni hassas bir polimerizasyon tipi olan atom transfer radikal polimerizasyonu, dar molekül ağırşığı dağılımı sağlaması açısından artan bir ilgi görmektedir. ATRP sisteminin değeri, sıradan bir polimerizasyon prosedürüyle gerçekleştirilebilir olmasıdır. Atom transfer radikal polimerizasyonun ismi, polimerik zincirlerin düzgün büyümesinin kilit noktası atom transfer basamağından gelmektedir. ATRP, atom transfer radikal eklenme (ATRA) reaksiyonlarından gelmektedir. Radikal oluşturmak için, bir organik halidden bir geçiş metal kompleksine atom transferi sağlar ve devamında nihai ürünü oluşturmak için geçiş metalinden ürüne geri radikal transferi sağlar. Atom transfer radikal polimerizasyonunun kontrollü zincir büyümesi, iyi tanımlanmış blok ve aşı kopolimeri hazırlanması çok kullanışlıdır.

Trifenil fosfin oksit içeren poli(metil metakrilat) iki fonksiyonlu bir başlatıcı olarak, N,N,N′,N″,N″-pentametildietilentriamin ligand olarak, bakır(I)bromür metal olarak, anizol çözücü olarak kullanılmış ve uçlarında spiropiran bulunan bir polimer ATRP ile sentezlenmiştir. Polimer, UV spektroskopisi, ^{1}H NMR spektroskopisi ve jel geçirgenlik kromatografisi ile karakterize edilmiştir.

1. INTRODUCTION

The molecular design and synthesis of photochromic materials have been well-studied because of their potential application such as opthalmic lenses, printing materials, information storage, signal transmission system, molecular switches, sensors, novelty items (toys, T-shirts), cosmetics [1].

Photochromic compounds can be incorporated into polymer matrices either by dispersing or covalently bonded to a polymer backbone [2].

Photochromic substances exhibit a reversible change when exposed to light radiation involving ultraviolet radiation. Generally, photochromic substances contain acrylate monomers are crosslinked by UV to form a photochromic coating film [3].

Spirobenzoyrans are a very widely studied chemical class of compounds which exhibit photochromism. Irradiation of the colourless spiropyran with UV light causes heterolytic cleavage of the carbon–oxygen bond forming the ring-opened coloured species called the merocyanine form [4].

Spirooxazines, the nitrogen containing analogues of the spiropyrans, are very resistant to photodegradation. This resistance to photodegradation, known in this field as fatigue resistance, is an essential property for those photochromic materials designed for applications in solar protection uses, e.g. in sun spectacles [4].

The controlled chain growth and living nature of ATRP make it very useful for the preparation of well-defined block and graft copolymers [5].

Stimuli responsive polymers have been investigated intensively as important elements for the development of smart materials and devices [6].

Of particular interest is to determine the minimum number of spiropyran units required in a polymer to trigger a measurable response. This also relates to the question of positioning of the spiropyran units in the polymer [6].

2. THEORETICAL PART

2.1 Photochromism

2.1.1 Introduction

Photochromism is a reversible transformation of a chemical species induced in one or both directions by absorption of electromagnetic radiation between two forms, A and B, having different absorption spectra.

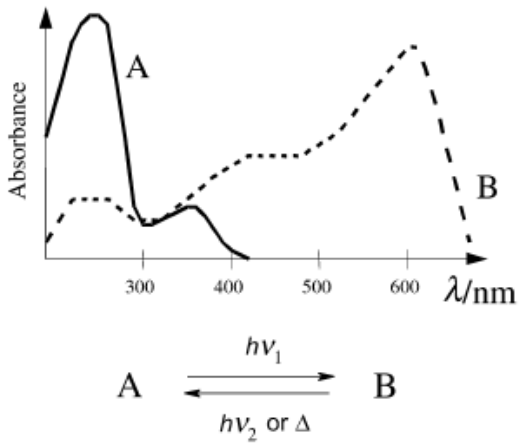

Figure 2.1 : Absorption spectra of A and B

The thermodynamically stable form A is transformed by irradiation into form B. The back reaction can occur thermally (Photochromism of type T) or photochemically (Photochromism of type P) [7,8].

The most prevalent organic photochromic systems involve unimolecular reactions: the most common photochromic molecules have a colorless or pale yellow form A and a colored form B (e.g., red or blue). This phenomenon is referred to as positive photochromism. Other systems are bimolecular, such as those involving photocycloaddition reactions. When $\lambda max(A) > \lambda max(B)$, photochromism is negative or inverse [7,8].

The unimolecular processes are encountered, for example, with spiropyrans, a family of molecules that has been studied extensively. Solid photochromic spiropyrans or solutions (in ethanol, toluene, ether, ketones, esters, etc.) are colorless or weakly colored. Upon UV irradiation, they become colored. The colored solutions fade thermally to their original state; in many cases, they can also be decolorized (bleached) by visible light. A few spiropyrans display negative photochromism. They are colored in the dark and bleached by UV light. Many spiropyrans are also thermochromic (see definition below), and spectra of the colored forms are identical to those produced photochemically [7,9].

2.1.2 Photochromic systems

The performance of physically dispersed and covalantly attached photochromic molecules in polymer matrices depends on the molecular structure, conformational changes, enviroment, and kinetic processes. Since there is no single molecule matrix pair that processes all these attributes, the search for newer materials with higher response speeds and fatique factor continues and is primarily driven by potential applications. While the specificity and complexity of the matrices are the main road blocks, individual photochromic entities and their molecular and electronic properties typically are grouped on the basis of their scientific and technological importance into azobenzenes, spiropyranes, diarylethenes, and fulgides [2,10].

2.1.3 Photochromic polymeric systems

Photochromic chromophores can be incorporated into polymer matrices either by dispersing them or covalantly attaching them to a polymer backbone, and many studies focused on the fundamental understanding of mechanisms governing photochromic polymers as well as on applications ranging from photoswitching to optical data-storage devices, sensors or light-driven reactors, and artificial muscles [2].

2.1.4 Spiropyrans

Spiropyrans are photochromic materials that exist in two forms: SP (colorless) and MC (colored) Figure 2.2 [2].

The MC form exhibits a characteristic absorption band due to extended π-electron conjugation in the visible region. In polar solvents, it exists in an yor all of the

following four complicated zwitterionic forms by changing its conformation about the conjufated bond: trans-transoid-trans (TTT), trans-transoid-cis (TTC), cis-transoid-cis (CTC), and cis-transoid-trans (CTT). Furthermore, MC exhibits a strong tendency to aggregate in stacks, giving the rise parallel (head-to-head, J-aggregates) and antiparallel (head-to-tail, H-aggregates) molecular dipoles. The open MC form converst back to the closed SP form either by irradiation in the visible region or by thermal exposure. Contrary to azobenzenes, where a number of reversible trans-cis isomerization cycles are possible without and degradation, in spiropyrans, the number of cycles is limited, thereby limiting the applicability. Knowledge of photochemicaland thermal processes in the ring opening and closure pathways lead to systems with better photochemical and thermal stability. The techniques applied include protanation of the MC-phenoxide moiety, synthetic modification of the SP with crown ethers, or a 7-trifluoromethylquinoline group, and by intramolecular bidenatte metal ion chelation [2-11].

Time-resolved spectroscopic studies provide useful information on the Dynamics and nature of intermediates involved in reversible photochemical and thermal ring openings as well as closure reactions in spiropyran compounds. As shown in Figure 2.2 the first step involves cleavage of the C-O bonds between the spiro carbon and the oxygen, followed by orthogonal SP to planar MC conversions. The C-O bond cleavage occurs on a timescale of picoseconds or even faster. It has been proposed that the mechanism of photochemical ring-opening reaction involves the immediate formation of a singlet excited state, intermediate species, or a metastable species in less than 100 fs. A part of the metastable species restores the initial C-O bond back-formation in a few picoseconds, and the remaining portion forms a mixture of transient MC conformers with a decay time constant of 100 ps. The mechanism of photochromic transformation of spiropyrans is shown Figure 2.2 [12-13].

The most common synthetic methods for designing spiropyrans involve condensation of a heterocyclic quaternary salt with an alkyl group at the vicinial position to the heteroatom or condensation of 2-hydroxyarenealdehyde with the corresponding heterocyclic methylene base. As a majority of bases have the tendency to dimerize, their use is undesirable during the synthesis. Benzothiazoline, benzodithiole, and benzopyrans can be synthesized by using alkylimmonium, oxonium, and thinium salts as precursors, respectively. One of the characteristic features of spiropyrans is a

strong absorption, maximum around the 290-380 nm regions due to the presence of benzopyran moiety. A number of attempts to incorporate spiropyran molecules into polymer systems have been reported, which include photochromic studies of spiropyrans in polymer matrices, liquid crystal polymers containing spiropyran as mesophases, and spiropyran-grafted dextran, pullulan, polydimethylsiloxane, and other synthetic polymers [14-15].

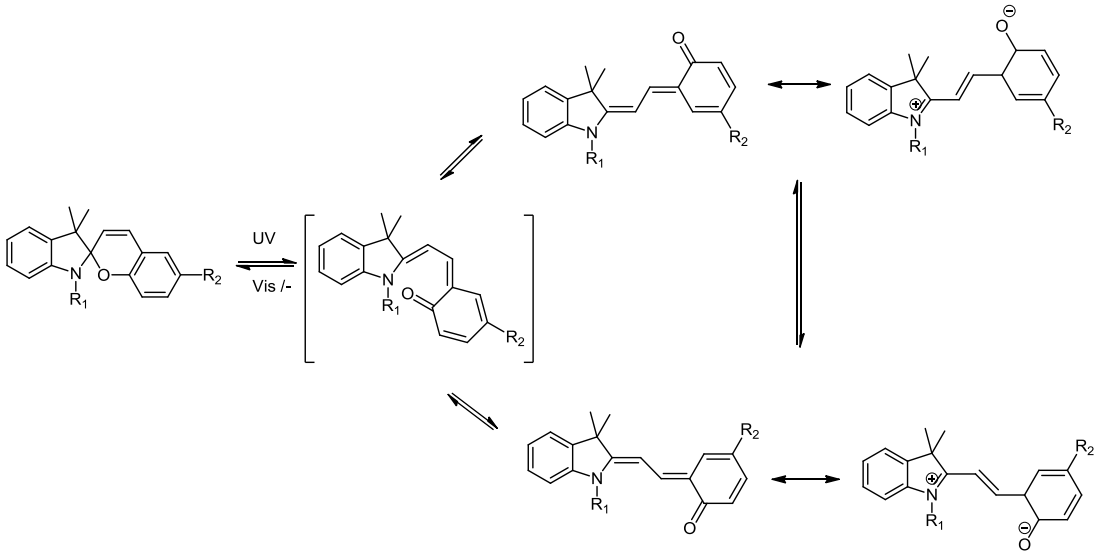

Figure 2.2 : Mechanism of ring-opening and ring-closing in spiropyrans

2.1.4.1 Solvatochromic properties of spiropyran

Crucial to all of the applications for which spiropyrans have found use is a detailed understanding of the kinetics of the transitions between the spiropyran (SP) and merocyanine (MC) forms. The conversion of SP to MC occurs via a photochemical route involving ultraviolet photons. The transition from SP to MC has been studied and determined to occur on the pico to nanosecond time scale and thus is too fast to follow using the instruments available for this experiment. Once irradiated with UV light, the ring opened, and colored MC form slowly rearranges back to the SP form. The color of the MC form as well as the rate of rearrangement back to the SP form are both dependent on the solvent polarity. The dependence of the rate of the back reaction on the polarity of the solvent arises from the zwitterionic MC form which is stabilized in polar solvents. The stabilization of the MC form in polar solvents leads to a larger energy of activation and a slower MC-SP transition as compared to non-polar solvents. The color dependence of the MC form (known as solvatochromism) arises from the difference in polarity between the photo-excited MC form and the

zwitterionic ground state MC form. For the case of 6-NO2-BIPS the excited state of the MC form is less polar than the zwitterionic ground state. In polar solvents the ground state of the MC form is stabilized relative to the excited state of the MC form leading to a blue shift in the absorption maximum as shown in Figure 2.3 below [16-18].

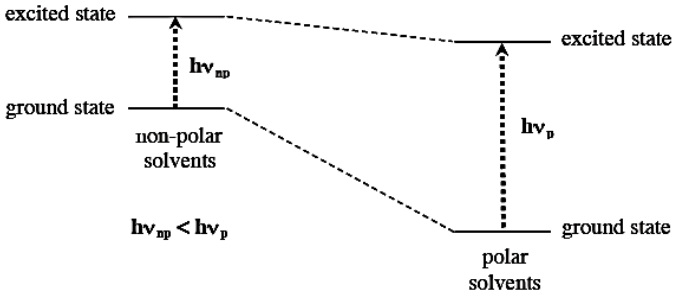

Figure 2.3 : Solvatochromic shift of the MC form

2.1.4.2 Applications of spiropyrans

Photochromic plastic ophthalmic sunglasses are the largest volume and value application for photochromics, but the indolinospiropyrans originally used generally underwent photodegradation (fatigued) rapidly in sunlight, a serious deficiency for this application. The emphasis then shifted to the spironaphthoxazines, which generally were more resistant to fatigue [19].

Spiropyrans are commercially used in moderate quantities as exposure indicators in photolithographic plates, in small quantities for microimage recording, and in a most interesting application, fluid-flow visualization. For these uses, fatigue is not an important limitation. In addition, relatively small amounts are used in printing inks for T-shirts and in toys and novelties having a limited lifetime [2].

One recent trend has been away from using a photochromic dye itself merely as an individual component of a solution, polymer film or bulk polymer matrix. Instead, the photochromic is chemically linked to a polymer, which may be a natural polymer such as a cellulose derivative, an enzyme, a protein, or synthetic polymers from acrylates, urethanes, and vinyl compounds. The properties of the polymer can then be modified by external irradiation, and conversely, the properties of the photochromic are modified by the polymer. A recent biochemical example is the photocontrolled binding of monosaccharides to concanavalin A (Con A) modified with spiropyran units [20].

A spiropyran-linked polymer is a polymer having photosensitive side chains; but to a dyestuff chemist, it is a spiropyran with a substituent that happens to be a polymer. The polymer modifies the properties of the spiropyran, and the behavior of the spiropyran gives information about the polymer. That the thermal fade rate of a spiropyran open form is much lower when it is bound to a polymer than when it is unbound is well–known. Conversely, a graph of fading rate constants vs. temperature showed breaks that may be attributed to a relaxation mode of the polymer chain [20].

A spiropyran is used as an orientated species. Dye in Langmuir-Blodgett films, in bipolar membranes, in liquid crystalline solvents, and adsorbed or vapor deposited on crystalline surfaces exhibits photochromic behavior significantly different from its behavior in dilute fluid solutions or amorphous polymer films or bulk matrices. In an indirect technique for controlling orientation, a silica surface is treated with a photochromic silylating reagent (a 6-nitroBIPS derivative) to give a command surface that when exposed to linearly polarized UV light causes the homogeneous alignment of adjacent nematic liquid crystals [2,20].

Spiropyrans show promise for optical recording, three-dimensional optical memories, and holography. The dyes currently under study for these applications very probably will not be used merely dissolved in a bulk polymer matrix, but will be oriented in films and membranes, or adsorbed or vapor deposited on solid substrates to take advantage of the nonlinear optical properties of the colored forms [22-24].

2.1.4.3 Synthesis of spiropyrans

The synthetic pathway to spiroindolinobenzopyrans illustrated in is representative of the methodology used to make this class of compounds. The parent spiroindolino compound is made by the condensation of the readily available Fischer's base with salicylaldehyde. The same route can be used with an indolinium compound bearing different N-alkyl groups and ring substituents; synthesised as shown in Figure 2.4. Substituted salicylaldehydes and also 2-hydroxynaphthaldehydes can also be used to give other analogues [4].

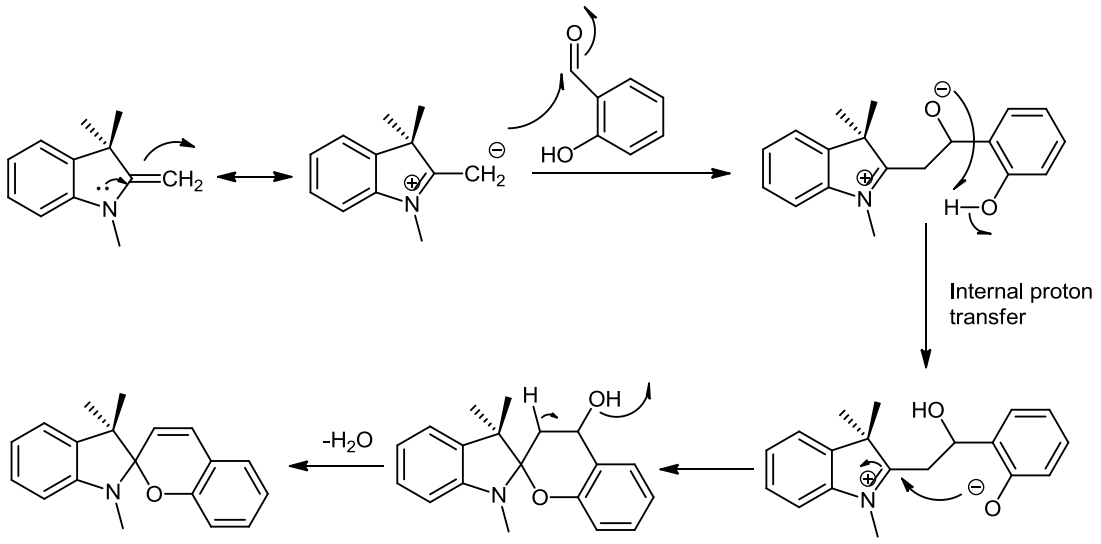

Figure 2.4 : Synthesis of spiropyran

2.2 Atom Transfer Radical Polymerization

As a novel precision polymerization, atom transfer radical polymerization (ATRP) has recieved rapidly increased interest recently, since it furnishes control over the resulting polymers, which posses narrower molecular weight distributions. The merit of the ATRP system is that it can be performed by an ordinary polymerization procedure. The name atom transfer radical polymerization (ATRP) comes from the atom transfer step, which is the key elementary reaction responsible for his uniform growth of polymeric chains. ATRP originates in atom transfer radical addition (ATRA) reactions. It employs atom transfer from an organic halide to a transition-metal complex to generate the reacting radicals, followed by back transfer from the transition metal to a product radical to form the final product [25,26,27].

2.2.1 Mechanism and kinetics of ATRP

ATRP was developed by designing a proper catalyst (transition metal compound and ligands), using an initiator with an appropriate structure and adjusting the polymerization conditions, such that the molecular weights increased linearly with conversion and the polydispersities were typical of a living process [28,29].

This allowed for an unprecedented control over the chain topology, the composition and the end functionality for a large range of radically polymerizable monomers.

A general mechanism for ATRP is shown in Figure 2.5. In ATRP technique, the halide (X) atom is produced from an activition of alkyl halide, the alkyl halide also

producing an alkyl radical initiator. This reaction is catalyzed by a complex formed between a transition metal compound such as CuBr or CuCl and ligands.

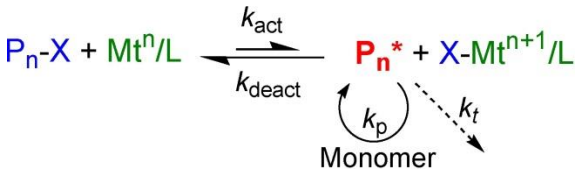

Figure 2.5 : General mechanism for ATRP

This process occurs with a rate constant of activation, ka, and deactivation kd, respectively. Polymer chains grow by the addition of the radicals to monomers in a manner similar to conventional radical polymerizations, with the rate constant of propagation, kp.

Termination reactions (kt) also occur in ATRP, mainly through radical coupling and disproportionation; however, in well-controlled ATRP, no more than a few percent of the polymer chains undergo termination.

Higher activation energy for the radical propagation than for the radical termination, higher kp/kt ratios and better control may be observed at higher temperatures.

The rate of polymerization is first order with respect to monomer, alkyl halide (initiator), and transition metal complexed by ligand. The reaction is usually negative first order with respect to the deactivatior (CuX2/Ligand).

The rate of law ATRP is formulated in discussed conditions and given in equation **2.1** [30].

$$R_p = k_p[M][P^\bullet] = k_p[M]K_{eq}[I]_o \frac{[Cu^I]}{[X\text{-}Cu^{II}]} \qquad \textbf{(2.1)}$$

2.2.2 Molecular weight and molecular weight distribution

As in typical living polymerization, the average molecular weight of the polymer can be predetermined by the ratio of consumed monomer and the initiator (DPn=Δ[M]/[I0]) while maintaining a relatively narrow molecular weight distribution (1.0<Mw/Mn<1.5) In addition, precise control over the chemistry and the structure of the initiator and active end group allows for the synthesis of end-functionalized polymers and block copolymers [31].

The molecular weight distribution M_w/M_n is the index of the polymer chain-length distribution. In well-controlled polymerization, M_w/M_n is usually less than 1.10 [30].

2.2.3 Temperature and reaction time

The rate of polymerization in ATRP increases with increasing temperature due to the increase of both the radical propagation rate constant the energy of activation for radical propagation is appreciably higher than that for termination be radical combination and disproportianition. Consequently, at higher temperatures the ratio kp/kt will be higher and therefore better polymerization control will be observed [27,39].

The most important effect of reaction time in ATRP occurs at higher conversions. At high monomer conversions, the rate of propagation is very slows down considerably; however, the rate of any side reaction does not change significantly, as most of them are monomer concentration independent [30].

2.3 Urethane Acrylates

The reaction of isocynate group with the hydroxyl group of an acrylic or methacrylic monomer (Figure 2.6) will give the corresponding urethane acrylate or methacrylate. If diisocynates are utilised, then acrylate di-functionality may be obtained. In contrast with epoxy acrylates, where only a few similar starting materials are available, urethane acrylates can be prepared from a large, diverse range of raw materials. This results in many possible variations in prepation and a very large range of properties of finished products. The isocynates which may be acrylated include toluene diisocynate (TDI), tetramethylxylene diisocynate (TMXDI), hexamethylene diisocyanate (HMDI), isophrene diisocynate (IPDI, and its chain isomer, trimethylhexamethylene diisocyanate (TMDI), dicyclohexylmethane diisocyanate (H12MDI), xyleen diisocyanate (XDI) and diphenylmethane diisocyanate (MDI). HMDI and TDI are extremely hazardous, being relatively volatile. To minimize this problem, oligomers of HMDI are used. TDI is reacted with a triol to give a relatively safe product. H12MDI consist of three stereoisomers because of the reduction of the aromatic MDI. Hydroxy functional monomers include hydroxyethyl acrylate (HEA), hydroxypropyl acrylate (HPA) and hydroxyethyl methacrylate (HEMA). If other hydroxyl containing compounds are also present, like polyethers, polyesters or

polyols that contain more than one hydroxyl group per molecule, then chain extension is possible. This results in a wide range of prepolymers that vary in functionality and molecular weight with correponding variations in film properties. Urethane acrylates probably offer a far wide range of final film properties than any other class of radiation curable oligomers [32].

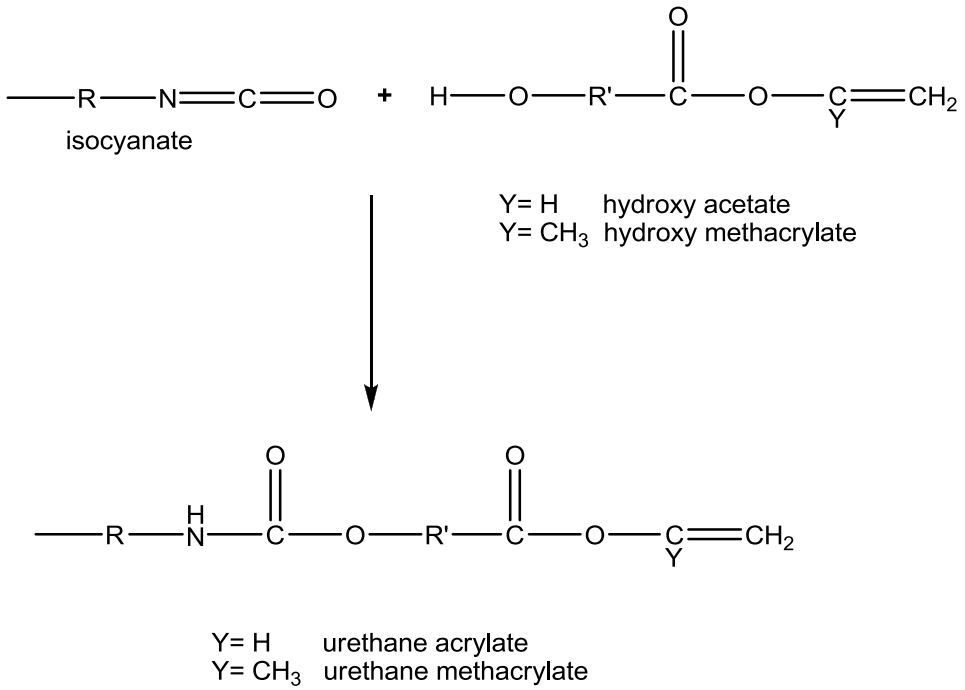

Figure 2.6 : Isocyanate-hyrdoxyl acrylate reaction

2.4 Phthalocyanines

Phthalocyanines have a two-dimensional 18 π -electron conjugated system, in which more than 70 different metal and also non-metal ions can be incorporated. A number of modifications can be made in the macrocycle either by introduction of different central ions or by substitution of functional groups at the peripheral sites of the ring. Moreover, the formal substitution of one or more isoindole units by another heterocycle affords the phthalocyanine analogues. Phthalocyanines can be also polymerized in one or two dimensional arrays. This architectural flexibility facilitates the tailoring of their properties over a very broad range. The preparation properties and applications of phthalocyanines have been recently reviewed [32].

Phthalocyanines have a great technological potential in areas related to intrinsic semiconductors and conducting polymers, nonlinear optics, chemical sensors,

electrochromic display devices, laser recording materials, information storage systems and liquid-crystal colour display applications, among other [33].

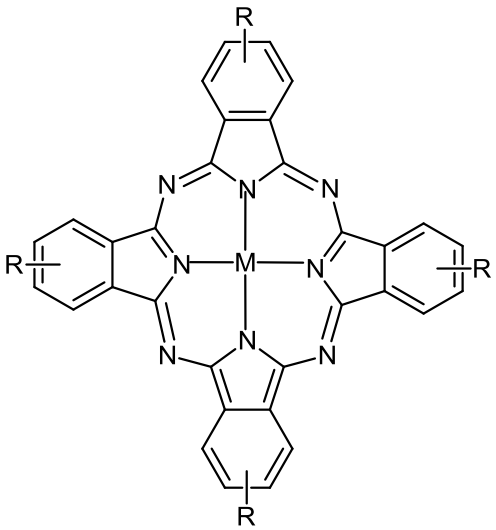

Figure 2.7 : Metallophthalocyanines

2.4.1 Phthalocynanine usage in photochromic system

Their useful properties are attributed to their efficient electron transfer abilities [34].

The ability of phthalocyanine and vanadyl phthalocyanines to form charge transfer complexes has been reported [15,16]. Phthalocyanine and porphyrins are also semiconductors. These properties might hint at the physico-chemical process that accelerates the photoreversion, and in particular explain why phthalocyanine and vanadyl phthalocyanines cause the greatest effect [35].

2.5 UV Coatings

2.5.1 Introduction to coatings technology

Coatings are found almost anywhere in daily life, the most prominent examples are architectural wall coatings and automotive paints. They are applied in order to provide:

a) decorative appearance, and/or

b) protective barrier.

The main functions of a coating are thus on the one hand to ensure the desired appearance (colour, gloss) and on the other hand the necessary protection, against corrosion, Stone chipping, scratches, abrasion or chemical attack, like red wine, coffee or mustard on furniture coatings or acid rain, tree resins or bird excrements on automotive coatings. Whereas the do-it-yourself architectural coatings are almost all water-based, the vast majority of industrially used coatings, applied in factories on various substrates, like vehicles, furniture, metal cans, paperboards, etc., still contain solvents. The coatings and application spectrum are predominantly based on the industrial coatings sector, which had a share of about 40% of the whole worldwide coatings market (60% architectural) [36,37].

2.5.2 UV Technology and applications

UV curing has now been established as an alternative curing mechanism to thermal hardening, contrary to the past, where it was only considered for the curing on temperature sensitive substrates, like wood, paper and plastics. This alternative curing technology uses the energy of photons of radiation sources in the short wavelength region of the electromagnetic spectrum in order to form reactive species, which trigger a fast chain growth curing reaction.

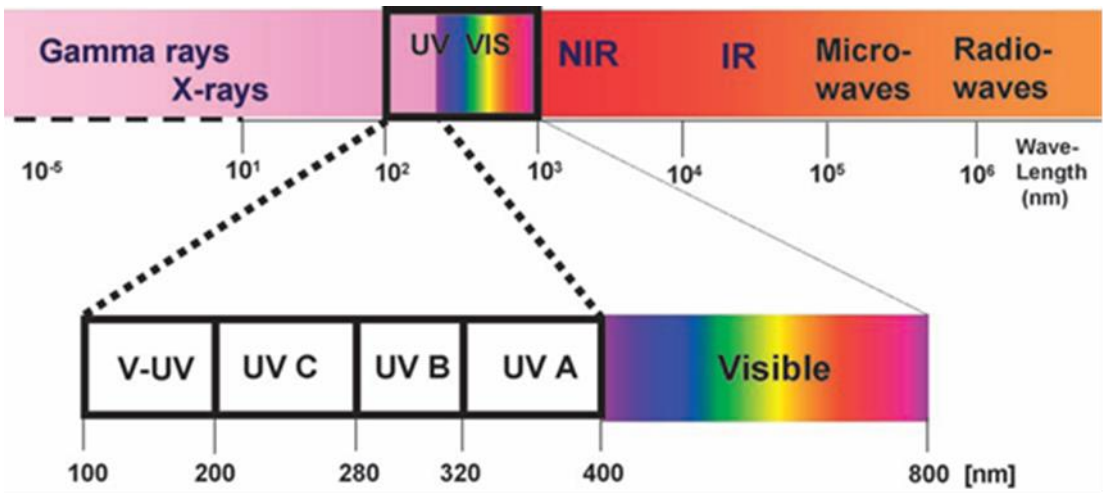

Figure 2.8 : Electromagnetic energy spectrum

Out of the electromagnetic spectrum (shown in Figure 2.8 is the range from the nearinfrared (NIR), over visible and ultraviolet (UV) to electron beams and X-ray) the UV region, further classified into UV-A, UV-B, and UV-C radiation, is mainly used for this technology. The energy content of a photon is defined by the equation;

$$E = h\nu = hc/\lambda \qquad \textbf{(2.2)}$$

where ν is the frequency and λ is the wavelength (nm). This equation tells us, that the shorter the wavelength, the higher the energy of a photon. UV light in the wavelength region of 300–400 nm should already be able to cleave C–C bonds. The high energy photons of e-beam and X-ray are sufficient to cleave C–C or C–H bonds, thus, they do not need a special photoinitiator for forming the desired radical species as initiators for polymerization. In the case of UV exposure, however, photoinitiators are commonly used, since the direct cleavage processes are not efficient enough. The photoinitiators are excited and after a cascade of reactions form the desired reactive species. In the case of using longer wavelength exposures, more complicated energy transfer reactions are needed. From the spectrum of usable radiation energy sources, UV technology is by far the most common one. From the higher energy radiation sources, e-beam technology has been widely explored for coatings technologies. It is still the most economical technology for industrial applications with very high volumes. However, the high safety requirements related to the use of e-beam technology and the high investment costs hamper the widespread use of this technology [37,38].

In UV curable lacquers, about 1–8% photoinitiators, as well as several other additives (from 1% up to 50%), like leveling agents, stabilizers, UV absorbers, radical scavengers, pigments and so on, are used to tailor the formulation to the application process and coating property requirements. This general composition of UV curable coatings applies to radically polymerizable coatings as well as to cationically curable systems and EB curable coating, which, however, do not need photoinitiators.

2.5.3 Advantages and drawbacks of UV coatings

Economical advantages are energy saving (commonly rapid cure at room temperature), high production speed, small space requirements and immediate post cure processing possible. Ecological advantages are in general solvent free formulations (VOC reduction), possibility of easy recycling (waste reduction) and energy saving. Performance advantages are low substrate heating, high product durability, application versatility, high scratch resistance and chemical resistance, exceptional abrasion, stain and solvent resistance and superior toughness.

Drawbacks are material costs are higher than, e.g., alkyds, polyesters or epoxies, 3D curing equipment development is in its infancy, UV curing in the presence of UV stabilizers decelerated, oxygen inhibition at the surface (in many radical curing systems), sensitivity to moisture (cationic curing system), difficult through-cure of pigmented coatings (at thicknesses >5 μm), topics to eliminate weaknesses, improving adhesion to metal, plastics, minimizing skin irritation caused by some reactive diluents, reducing odor (of the formulations), reducing extractables of cured coatings, improving photoinitiators (cost, migration, volatility) and direct food contact packaging approval [36].

2.5.4 The UV curing process

The UV curing process is predominantly determined by the desired application of the coating. The intended end-product governs the substrate to be coated. This may be an abrasion resistant clear coat for ready-to-install parquet or an overprint varnish for paper cards, a coloured base coat and a clear coat for plastic automotive parts or metal coils, as well as a flexible protective coat for window frames. The function of the coating, for instance the colouration of the part, the protection against corrosion, scratching, chemical attack or against weathering deterioration, determines the type and property requirements of the coating as well as the thickness required. The targeted properties, like high gloss appearance, abrasion resistance, colour effects, hardness, flexibility, resistance against chemicals or scratches, have to be provided by the chemical formulation, consisting of base resins, diluents, photoinitiators and various additives. Furthermore, an appropriate selection of the components has to be done in order to enable an effective curing process; for instance, in coatings containing pigments or UV light stabilizers, the spectral absorbance of the photoinitiator has to be adjusted to a spectral region where the pigments or UV absorbers are fairly transparent. This fine tuning is necessary to match the characteristics of the lamp system with the chemistry of the coating to provide an economic curing process. Besides the physical properties of the cured material to be obtained, the economics of the coating process is the most important variable which decides over the type of coating used. Thus, in order to calculate the total costs of a coating process, not only materials costs but the whole process design and the equipment set-up have to be considered in order to compare different coating processes with each other. UV curable coatings are always in competition with

thermally curable systems of the classical solvent-type, water-based or powder coatings. Some economic factors of UV curing have been discussed with cost examples for ink, coating and adhesive applications in comparison with thermal hardening, if applicable. UV curing in general offers a number of advantages over competitive coatings, while some can be related to costs, others relate to performance, environmentally compliance or processes not achievable with other methods.

Thus, the UV curing process relies crucially on an efficient cogging of the required application properties with the chemistry chosen to fulfill the performance requirements as well as the UV curing equipment applied to provide a fast and complete cure in order to meet the economical and ecological aspects of coating technology. UV curing in its basics is a fast, room temperature curing process indicating low energy consumption and requiring little space for the equipment [38].

2.5.5 The photochemical process

2.5.5.1 Photoinduced curing chemistry

Photoinduced curing can be realized as in the preparation of conventional linear polymers by a step like process, as used in polyaddition and polycondensation reactions or by a chain process occurring in polymerization reactions.

The photoinduced polyaddition technology has been for a long time the workhorse of photoresist technology, for example, the crosslinking of resins was achieved by photoinduced dimerization of cinnamates. This photodimerization is an example of a direct photoreaction where every step of polymer built-up is initiated by an absorbed photon, thus every single reaction step is dependent on the quantum yield of the photoreaction (generally very much smaller than 1). On the contrary, in polymerization reactions induced by light only the initiating step is dependent on the photoreaction ($\Phi < 1$). The photopolymerization reaction then is a chain reaction, where one produced initiator radical can add up to several thousand monomer units, thus the overall quantum yield of the total reaction is much bigger than 1. Whereas the photoinduced radical polymerization is now the mainstream technology, the photoinduced ionic curing reactions are not so well explored and developed, mainly due to the lack of easily available photoinitiators [55-57]. The basic principles of curing and network formation are similar in radical and cationic induced curing. The

cationic curing has its main advantages in the oxygen insensitive curing and in the good adhesion mainly to metals achieved with the cationic curable epoxy systems. The UV curing technology is based on the photoinitiated rapid transformation of a reactive liquid formulation into a solid coating film. The initiating species may be a cation, an anion or a radical. The vast majority of UV curable coatings are based on radical producing photoinitiators. The main components of such formulations based on radical polymerizations are reactive resins containing a plurality of polymerizable double bonds, which govern mainly the desired properties of the final coating; copolymerizable, monomeric diluents, which are responsible for the reduction or adjustment of the viscosity of the formulation, a function taken by the solvent in conventional formulations; photoinitiators or a photoinitiating system containing photoinitiator and photosensibilizer or coinitiators; and, if necessary, other coating additives, like surface active additives, slip additives, fillers, pigments, light stabilizers, etc. The chemistry involved in the radical initiated UV induced crosslinking can be divided into the three steps, initiation, propagation and termination. Although the UV energy applied in photocuring may cleave C–C and C–H bonds, the commonly used monomers do not produce sufficient amounts of initiating species, which is due to low absorbance and poor cleavage efficiency. Thus, a special photoinitiator is usually applied, which is excited and ultimately yields via intersystem crossing, accompanied by various deactivation reactions, the formation of a radical species, which can initiate radical polymerization. The following polymerization reaction follows almost exactly the rules of conventional radical polymerization. Thus, only the initiation step is different to thermal initiated radical polymerization. The light absorption and the following processes are outlined in a Jablonski diagram. The process starts with the absorption of a photon by the photoinitiator molecule, which results in excitation of an electron into higher singlet states [39-41].

From these excited states, various processes can follow. First, deactivation can proceed by radiationless internal conversion and evolution of heat back to the ground state or by emission of fluorescence. Second, by intersystem crossing (ISC) an electron spin inversion leads to the excited triplet state. The photochemical processes which lead to the desired active species (e.g., free radicals) often take place from the excited triplet state, where the molecule posses two unpaired electrons, rather than

from the singlet state. The formation of the reactive species, namely free radicals, competes with further deactivation processes, like monomer quenching, oxygen quenching and phosphorescence. The direct oxygen quenching of the photoinitiator excited states is not very likely in the case of the extremely shortlived triplet states of α-cleavable type photoinitiators, but much more pronounced in the hydrogen abstraction type owing to the relatively long-lived triplet states. From the triplet state two main reactions can lead to initiating species, the intramolecular scission of an α-bond, or the intermolecular abstraction of a hydrogen atom. The intramolecular scission is the most effective process in the formation of radicals, since the hydrogen abstraction is a bimolecular type reaction, which is diffusion controlled and may be accompanied by several deactivation reactions. The quantum yield of initiation, representing the number of growing chains per photon absorbed reflects the importance of the processes leading to initiation over all the indicated processes of deactivation. The efficiency of the photoinitiation is a function of different quantum yields, since several side reactions can occur in every step. Thus, the overall yield of initiation is a complex function of different quantum yields, represented exemplarily. Propagation is the key step to very efficient curing, since it is a chain reaction where for instance one produced radical can add more than 1000 monomer units within a fraction of a second. The steps after the initiation are very similar to the normal radical polymerization of monofunctional monomers, which are widely used to synthesize thermoplastic polymers, like polyethylenes, polypropylene or polystyrenes. The main difference in coating systems is the use of multifunctional monomers or oligomers, which leads to the formation of networks. In the propagation reaction transfer reactions also often play a significant role, where the growing radical chain does not add to another monomer unit, but abstracts hydrogen radical from a neighbouring R–H group. The remaining radical can then start another growing chain, thus leading to the termination of the growing polymer chain, but not to the termination of the chain reaction. The reaction of the radicals with oxygen does not play a significant role in the polymerizations of linear polymers, since they are normally conducted under inert conditions. However, the curing of coatings is normally performed under atmospheric conditions, thus, the oxygen interference plays a major role. The termination reactions are also manifold. Besides the termination with an initiator radical, several other termination reactions play a role,

especially the recombination of growing radical species or elimination reaction of the chain end [42].

3. EXPERIMENTAL PART

3.1 Materials

For synthesis of 2-(3’,3’-dimethyl-6-nitrospiro[chromene-2,2’-indolin]-1’-yl)ethanol, 2,3,3-trimethylindolenine (Sigma-Aldrich), 2-bromoethanol, Potassium hydroxide (Merck), Acetone (Carlo Erba), Ethanol (Carlo Erba) were used.

For synthesis of 2-(3’,3’-dimethyl-6-nitrospiro[chromene-2,2’-indolin]-1’-yl)ethyl acrylate, 2-(3’,3’-dimethyl-6-nitrospiro[chromene-2,2’-indolin]-1’-yl)ethanol, Acryloyl chloride (Merck), Triethylamine (Acros), Dichloromethane (Merck) were used.

For synthesis of spiropyran bearing urethane acrylate, 2-(3’,3’-dimethyl-6-nitrospiro[chromene-2,2’-indolin]-1’-yl)ethanol, isocynate bearing urethane acrylate (Bayer), Dibutyltindilaurate (DBDTL), and Acetone (Merck) were used.

For synthesis spiropyran end functionalized polymer, triphenyl phosphine oxide containing PMMA (macroinitiator), 2-(3’,3’-dimethyl-6-nitrospiro[chromene-2,2’-indolin]-1’-yl)ethyl acrylate (monomer), Cupper(I)bromide (CuBr, metal, Aldrich), N,N,N′,N″,N″-Pentamethyldiethylenetriamine (PMDETA, ligand, Aldrich), and Anisole (Acros) were used.

For UV cruring formulations, Dipropyleneglycoldiacrylate (DPGDA, Cytec Chemicals), 1,6-hexandioldiacrylate (HDDA, Sartomer Chemicals), Irgacure 184 (Ciba Chemicals) and Photomer 6217 (Cognis) were used. Also phthalocyanine and 5-Chloro-1,3-dihydro-1,3,3-trimethylspiro[2*H*-indole-2,3′-(3*H*)naphth[2,1-*b*](1,4)oxazine] (SO, Aldrich).

A metal free phthalocyanine (F) which was used for film formulations was shown in Figure 3.1.

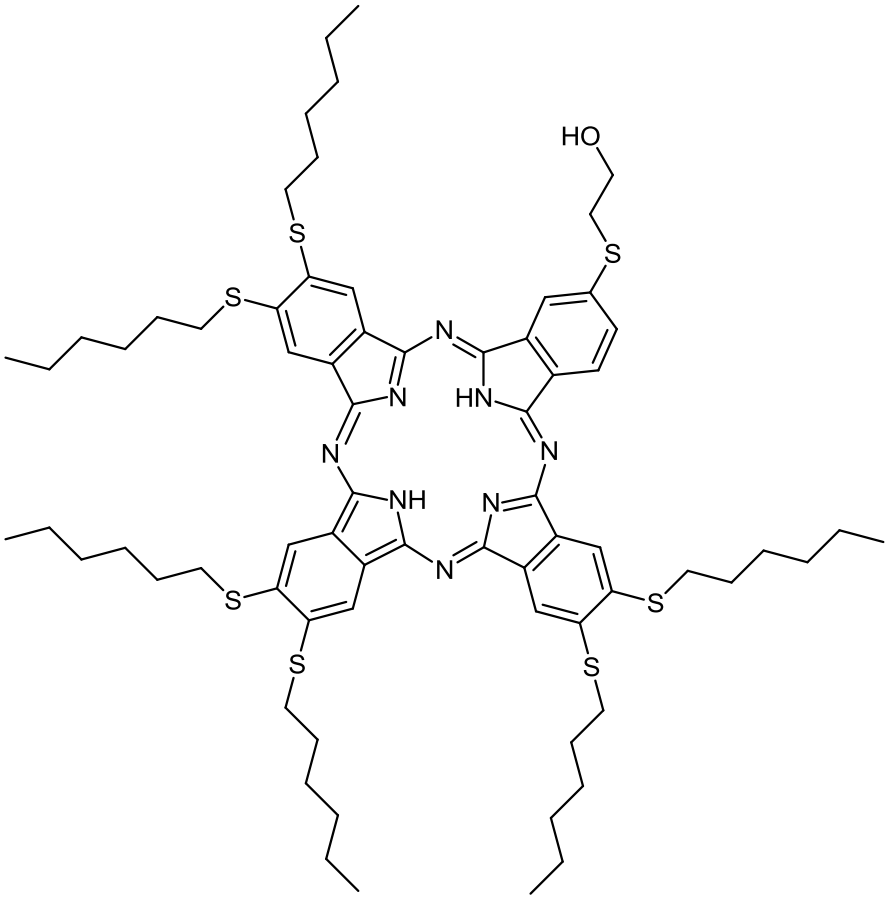

Figure 3.1 : Metal free phthalocyanine (F)

A commercial spirooxazine (SO) which was used for film formulations was shown in Figure 3.2.

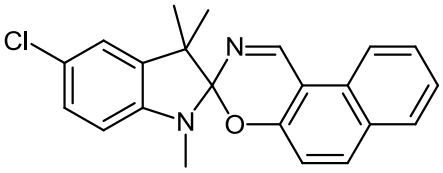

Figure 3.2 : Spirooxazine

3.2 Equipments

3.2.1 Infrared analysis (IR)

Infrared analyses were performed with Thermo Scientific Nicolet IS10 FT-IR spectrometer.

3.2.2 Nuclear magnetic resonance (NMR)

^{1}H-NMR analyses were performed with a Bruker 500 MHz Spectrometer.

3.2.3 UV spectroscopy analysis

UV spectroscopy analyses were performed with Shimadzu PharmaSpec UV-1700 UV-Visible Spectrophotometer.

3.2.4 Contact angle meter

The contact angles of cured films were measured by KSV CAM 100 instrument.

3.2.5 Pendulum hardness tester

A König Pendulum Hardness (BYK-Gardner) tester was used to measure the film hardness of films.

3.2.6 Tensile loading machine

Instron 3345 Universal Tensile Tester was used to determine properties such as modulus, elongation at break and strength.

3.3 Synthesis

3.3.1 Synthesis of 2-(3',3'-dimethyl-6-nitrospiro[chromene-2,2'-indolin]-1'-yl)ethanol (SP)

It was synthesized in two steps according to literature [43].

3.3.1.1 Synthesis of 1-(2-hydroxyethyl)-2,3,3-trimethyl-3*H*-indol-1-ium bromide

A solution of 2,3,3-trimethyl-3*H*-indole (12,5 mL) and 2-bromoethanol (7 mL) in 60 mL acetone was placed in a 250 mL three-necked round bottom flask equipped with nitrogen inlet, thermometer, $CaCl_2$ tube and condenser. The mixture was heated under reflux for 24 h. After cooling to ambient temperature, precipitated solid was filtered and wash with acetone many times. The resulting product was pink solid. The yield of the reaction was 71% and its melting point was 195^{o}C.

3.3.1.2 2-(3',3'-dimethyl-6-nitrospiro[chromene-2,2'-indolin]-1'-yl)ethanol (SP)

A solution of 1-(2-hydroxyethyl)-2,3,3-trimethyl-3H-indol-1-ium bromide (15.7 g) and potassium hydroxide (4.95 g) in 250 mL water was stirred at ambient temperature for 1 h. Then, 9,9,9a-trimethyl-2,3,9,9a-tetrahydrooxazolo[3,2-a]indole was extracted with dichloromethane (2x100 mL). The organic phase was dried over $MgSO_4$, filtered and concentrated under reduced pressure to afford a yellow oil.

A solution of 2-hydroxy-5-nitrobenzaldehyde in 75 mL absolute ethanol was placed in a 250 mL three-necked round bottom flask equipped with nitrogen inlet, thermometer, $CaCl_2$ tube and condenser. The mixture was heated about 74 ^{o}C. The oil was dissolved in 25 mL absolute ethanol and was added dropwise over 30 minutes. The mixture was heated under reflux for 24 h. After cooling to ambient temperature, precipitated solid was filtered and wash with ethanol many times. The resulting product was purple solid as 68% yield.

3.3.2 Synthesis of 2-(3',3'-dimethyl-6-nitrospiro[chromene-2,2'-indolin]-1'-yl)ethyl acrylate (VSP)

Under nitrogen, acryloyl chloride (1.3 mL) was added dropwise to a stirring mixture of 2-(3',3'-dimethyl-6-nitrospiro[chromene-2,2'-indolin]-1'-yl)ethanol (5g) and

triethylamine (2.86 mL) in 50 mL dichloromethane in ice bath for 1 h. After complete addition, the reaction was stirred at room temperature for 24 h. The reaction mixture was with 100 mL 0.5 M NaOH, 100 mL water, 100 mL 0.5 M HCl, 100 mL water, 100 mL brine and dried with $MgSO_4$. The solution was rotary evaporated (70% yield). [44]

3.3.3 Synthesis of spiropyran bearing urethane acrylate (SP-UA)

Under nitrogen, 0.2 g SP and 5 mL acetone were in a 50 mL three necked round bottom flask. 0.3 g isocyanate bearing urethane acrylate in 5 mL acetone was added dropwise to the solution over 20 minutes. The dibutyltinlaurate was added as catalyst. The reaction was continued till until the NCO peak at 2270 cm^{-1} disappeared totally in the FTIR spectra. The peak disappearance was controlled by samples taken from the reaction medium every 0.5 h. The final product was vacuum dried at ambient temperature.

3.3.4 Synthesis of spiropyran end fuctionalized poly(methyl methacrylate) via ATRP

To a schlenk tube equipped with magnetic stirrer, vacuum and dry nitrogen was applied 3 times, then 0.5 g VSP, 1.76 mg copper(I) bromide, 5.14 μL ligand (PMDETA), and macroinitiator 0.12 g triphenyl phosphine oxide containing PMMA [45] were added under nitrogen respectively. 2 mL anisole was used as solvent. The reaction solution was bubbled by nitrogen to remove dissolved gases and then the tube was immersed in an oil bath and held by thermostate 85 oC. The polymerization was performed for 48 h and terminated by cooling to room temperature. The reaction mixture was dissolved in large amount of THF. The THF solution was passed through a short alumina column to remove copper complex and then concentrated by evaporation. The polymer was precipiated into excess methanol and filtered. The filtrate was dried under vacuum. The conversion was determined gravimetrically. Mn: 12856, 32% conversion.

3.4 Preparations of Film Formulations

Nine different formulations were prepared for polymerization system.

Four different photochromic structure were used for formulations. Three of them were spiropyran based and the other one spirooxazine. Phthalocynanine was also used in each photochromic component formulations.

The composition of formulations are shown in Table 3.1.

Table 3.1 : UV curing formulations.

Sample / (wt. %)	F1	F2	F3	F4	F5	F6	F7	F8	F9
Urethane Acrylate	65	64.9	64.9	64.9	64.9	64.9	64.9	64.9	64.9
HDDA	10	10	10	10	10	10	10	10	10
DPGDA	20	20	20	20	20	20	20	20	20
Irgacur184	5	5	5	5	5	5	5	5	5
VSP	-	0.1	-	-	-	0.1	-	-	-
SP-UA	-	-	0.1	-	-	-	0.1	-	-
SP	-	-	-	0.1	-	-	-	0.1	-
SO	-	-	-	-	0.1	-	-	-	0.1
F	-	-	-	-	-	0.01	0.01	0.01	0.01

3.4.1 Preparation of test samples

3.4.1.1 Free films

Free film formulations were prepared according to the Table 3.1. Solutions were kept under vacuum approximately 30 minutes to remove bubbles. Then the formulations were applied onto glass plates using a bar gauged wired applicator obtaining a layer thickness of 30 μm and 120 μm.

3.4.1.2 Coated plexiglass plates

1g of film solution for each plates was prepared. Then the formulations were applied onto Plexiglass plates using a bar gauged wired applicator obtaining a layer thickness of 30 μm. Finally plexiglass plates were cured under EMA UV machine in analogy to free films UV curing way. Pencil hardness, contact angle and pendulum hardness tests were applied on these plates.

3.5 Analyses

Following tests; Infrared Analysis (IR), Nuclear Magnetic Resonance Spectroscopy (NMR), Ultraviolet-Visible Spectroscopy, Pendulum Hardness, Contact Angle Measurement, Tensile tests, Pencil Hardness, and Gel Content were performed to monitor morphological and film properties.

3.5.1 Infrared analyses

Infrared spectroscopy (IR) is used in the areas of determination of molecular structure, identification of chemical species, quantitative/qualitative determination of chemical species, and in a host of other applications.

This technique is used in the investigation of matter in the solid, liquid, and gaseous states. The application of IR is well known in the fields of chemistry, physics, materials science, etc. If a molecule is placed in an electromagnetic field (e.g., light), a transfer of energy from the field to the molecule will occur only when Bohr's frequency condition is satisfied.

$E = h\nu$

where,

h = Planck's constant

v = frequency of light

In the case of a diatomic molecule, it can be proven from mechanical considerations that the vibrations of the two nuclei in a diatomic molecule are equivalent to the motion of a single particle of mass, μ, whose displacement from its equilibrium position is equal to the change of the internuclear distance. The term μ is called the *reduced mass* and is given by:

$1/\mu = 1/m_1 + 1/m_2$

where, m_1 and m_2 are masses of the two nuclei.

The infrared vibrational spectrum of a molecule consists of a series of bands, each of which results from a transition between pairs of vibrational levels associated with the ground electronic state. With the help of quantum mechanics, the probability of a vibrational transition of a molecule can be obtained. The variation of the dipole moment vector can be expanded in a series in terms of the normal coordinates [46].

3.5.2 Nuclear magnetic resonance analysis

NMR observes radio frequency signals from atomic nuclei occupying excited spin states, and understanding the observations is best accomplished though a combination of the quantum mechanical and classical descriptions of the phenomena. NMR active nuclei are considered to have a quantized property called spin, which can usefully be thought of as being caused by physical spinning of the nucleus. The angular momentum, J, of such a nucleus is given by:

$J = h\,[I(I + 1)]^{½}$

where h is Planck's constant/2π and I is the spin quantum number which can be either an integer or half-integer. Nuclei with even mass number and even charge (e.g., 12C, 16O) have zero spin and are of no interest to NMR spectroscopy. Nuclei with odd mass numbers (e.g., 17O, 27Al, 29Si) have half-integer spins and are of most interest here. Nuclei with even mass numbers and odd charge (e.g., 2H, 14N) have integer spins and can be more difficult to examine, but can also be of considerable importance. Most nuclei have spins between 0 and 9/2. The magnetic moment of a nucleus is a fundamental property.

Each nucleus has $2I + 1$ spin energy levels which take on the values I, $I - 1$, $I - 2$, ..., $-I$. In the absence of a magnetic field, these energy levels are degenerate (have the same energy), but when a magnetic field is present this degeneracy is lifted. The chemical shift corresponding to the isotropic shielding is called the isotropic chemical shift, *i*, and has units of ppm. More negative or less positive chemical shifts correspond to larger shieldings. In many cases, the isotropic chemical shift is the most useful NMR parameter for structural investigations [47].

3.5.3 Gel content measurement

A cured film sample (m_1) was accurately weighted, and then added to the Soxhlet extractor with acetone as extraction agent for 6 hrs. The cured film was dried until its weight was constant (m_2). Gel content of the cured film was calculated by equation,

Gel content (%) = $(m_2/m_1) \times 100\%$

Where m1 is the weight of the cured film sample; m^2 is the residual weight of the cured film sample.

Solvents used in this test and results are shown in the Table 4.2.

3.5.4 Contact angle measurement

The contact angle is an important parameter in surface science. It is a common measure of the hydrophobicity of a solid surface In the past several decades, numerous techniques have been used to measure contact angle which were inspired by the idea of using the equation first derived by Thomas Young in 1805. Young's equation governs the equilibrium of the three interfacial tensions and the Young contact angle of a liquid drop on a solid. The derivation of Young's equation assumes that the solid surface is smooth, homogeneous and rigid; it should also be chemically and physically inert with respect to the liquids to be employed. Ideally, according to Young's equation, a unique contact angle is expected for a given system a liquid drop on a solid surface. In a real system, however, a range of contact angles is usually obtained instead. The upper limit of the range is the advancing contact angle which is the contact angle found at the advancing edge of a liquid drop. The lower limit is the receding contact angle which is the contact angle found at the receding edge. The difference between the advancing and receding contact angles is known as the contact angle hysteresis [47].

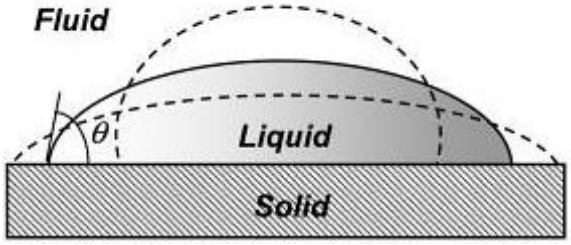

Figure 3.3 : Scheme of a sessile-drop contact angle system

The water contact angle of films prepared in are listed in Table 4.3.

3.5.5 Pendulum hardness test

Standard hardness tests relate oscillation damping to surface hardness. The Konig test for hard coatings measures the time taken for the amplitude to decrease from 6° to 3°. It uses the damping properties of organic surfaces (e.g., paints, coatings, plastic materials, films of all kinds, and paper) to determine the hardness. In its operation, the oscillations of a standard pendulum supported on the test surface by balls are dampened more strongly on softer surfaces. The degree of dampening is measured by the time in seconds taken for the amplitude of the pendulum to diminish from the initial to the final value [48]. It is described in the ISO Recommendation 1522 as follows [49]:

The pendulum rests on two stainless steel balls, 5 ± 0.005 mm diameter, of hardness HRC 63 ± 3, 30 ± 0.2 mm apart, and is counterpoised (to adjust the naural frequency of oscillation) by means of a weight sliding on a vertical rod attached to a cross bar. The period of oscillation should be 1.4 ± 0.2 s on a polished plate glass panel; the time for damping from a 6o displacement to a 3o displacement, o the same substrate, should be 250 ± 10 s. The total weiht of the pendulum should be 200 ± 0.2g.

The pendulum hardness of films prepared are listed in Table 4.4.

3.5.6 Pencil hardness test

ASTM Test Method for Film Hardness Test (D3363) is practical for laboratory use, for use on a production line, or in the field to assess quantitatively the rigidity or firmness (elastic modulus) of organic coatings applied to rigid substrates such as metal or plastic. Hardness values may define requirements for particular coating applications or may be used to evaluate state of cure or aging of a coating.

In this test, pencil leads of increasing hardness values are forced against a coated surface in a precisely defined manner until one lead marks the surface. Surface hardness is defined by the hardest pencil grade which fails to mark the organic coating surface.

Pencils are available in different grades of hardness, ranging form the softest, and 6B, to the hardest. 6H, although harnesses greater than 6H have been available.

Pencil leads are blends of graphite, clay, and binders. They range in hardness from softest to hardest as follows [48]:

6B, 5B, 4B, 3B, 2B, B, HB, F, H, 2H, 3H, 4H, 5H and 6H.

The results are shown in Table 4.5.

3.5.7 Tensile test

The tensile test serves as the basis for determining several important mechanical properties of materials. In this test, the yield strength, tensile strength, elongation, and reduction in area of a material specimen are determined. In addition, the modulus of elasticity, modulus of resilience, and modulus of toughness of a material are found from the stress–strain curve measured during the tensile test. In the tensile test the specimen is loaded in uniaxial tension until the specimen fractures. Because of the difficulty in determining the elastic limit, it is commonly replaced by the proportional limit, which is the stress at which the stress–strain curve is out of linearity. The modulus of elasticity, or Young's modulus, E, a measure of the stiffness of the material, is the slope of the curve below the proportional limit. The increase in load that occurs in some materials after the yield strength is reached is known as strain hardening or work hardening. Poisson's ratio ν is the absolute value of the ratio of the transverse strain to the axial strain of a specimen under uniformly distributed axial stress below the elastic limit. The specimen for a Poisson's ratio tensile test is of rectangular cross section.

The tensile strength of the material is calculated by dividing the maximum applied load by the initial undeformed cross-sectional area of the specimen. According to their ability to undergo plastic deformation under loading, materials are identified as being ductile or brittle. In a brittle material, fracture can occur suddenly because the yield strength and tensile strength are practically the same. The elongation and

reduction of area give an indication of the ductility of a material specimen, and the modulus of toughness shows the energy-dissipating capacities of the material, but both ductility and capacity for energy absorption are influenced by such factors as stress concentration, specimen size, temperature, and strain rate. A normally ductile material such as mild steel will behave in a brittle manner under conditions of low temperature, high strain rate, and severe notching. On the other hand, normally brittle materials will behave ductile under high hydrostatic pressures and temperatures. Therefore, assessment of the ductility and energy-absorbing capacity of a material must be made by taking into consideration the service conditions of the final product. [50].

The results are shown in Table 4.6.

4. RESULTS AND DISCUSSION

4.1 Synthesis of 2-(3',3'-dimethyl-6-nitrospiro[chromene-2,2'-indolin]-1'-yl)ethanol (SP)

It was synthesized in two steps according to procedure mentioned in section 3.3.1 [43] in figure 4.1.

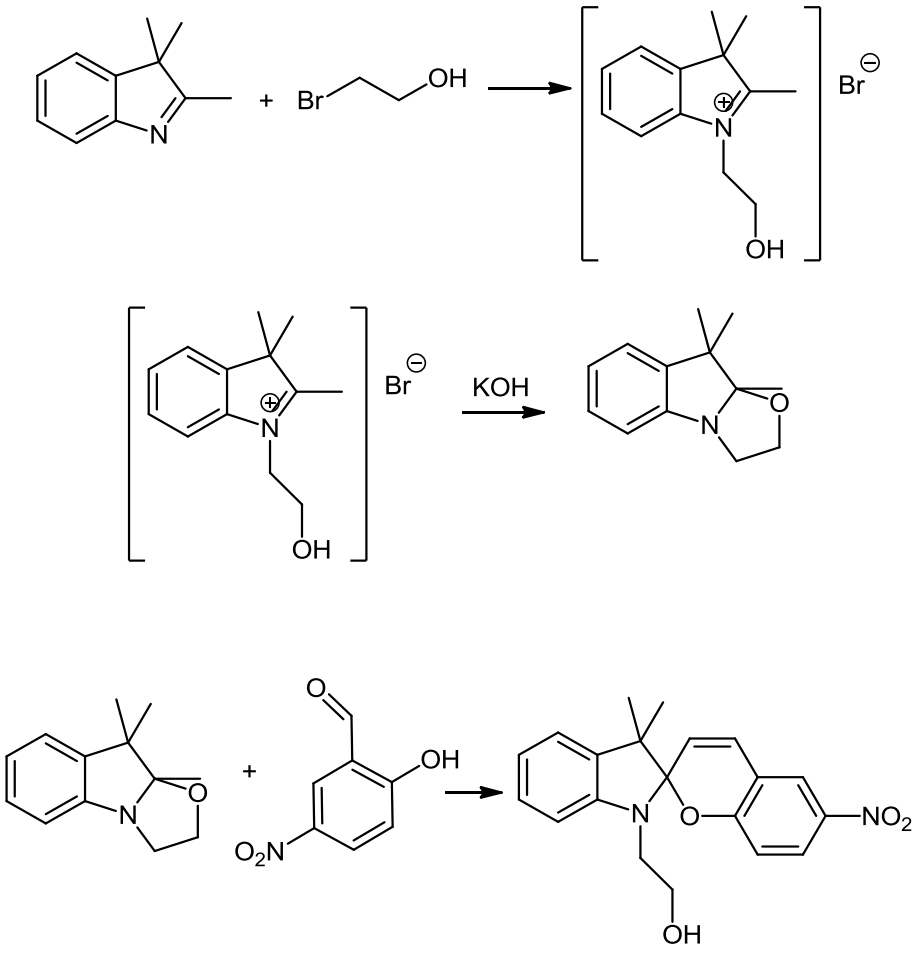

Figure 4.1 : Synthesis route of SP

The FT-IR spectrum of SP in Figure 4.2 contains charactheristic pyran ring peak at 1651 cm^{-1}, -CH_2-OH at 3333 cm^{-1}, -CH at 2924 cm^{-1}, -NO_2 at 1610 cm^{-1}, 1509 cm^{-1}, COC==C at 1479 cm^{-1}, 1333 cm^{-1}, 1273 cm^{-1}, 1022 cm^{-1}.

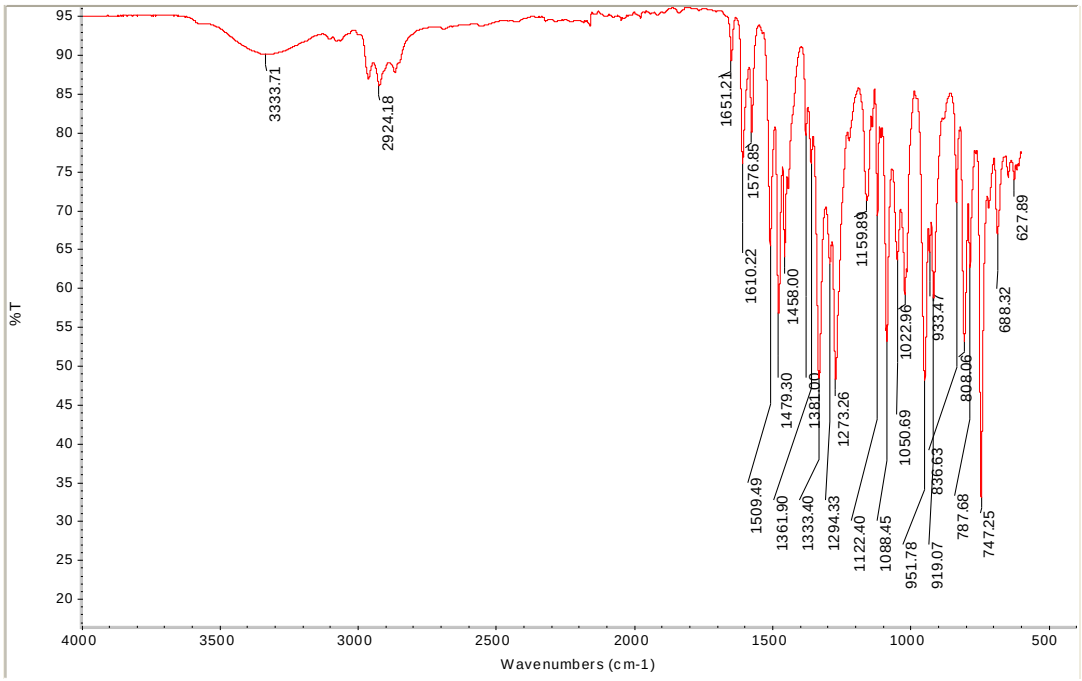

Figure 4.2 : FT-IR spectra of SP

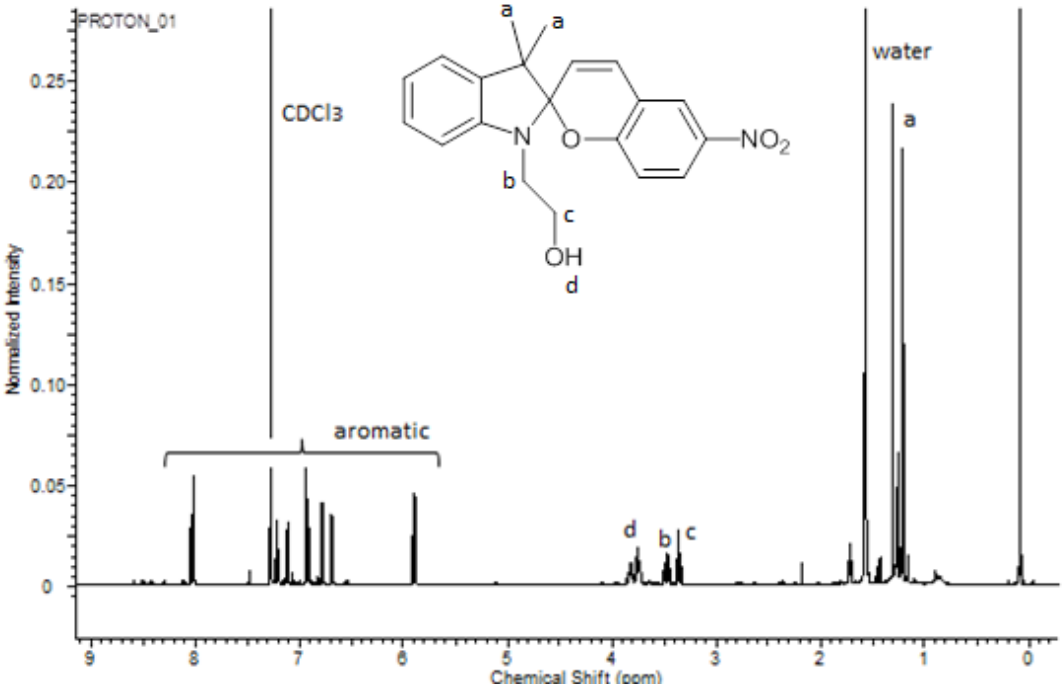

Figure 4.3 : ^{1}H NMR Spectrum of SP

4.2 Synthesis of 2-(3',3'-dimethyl-6-nitrospiro[chromene-2,2'-indolin]-1'-yl)ethyl acrylate

It was synthesized according to procedure mentioned in section 3.3.2 in Figure 4.4.

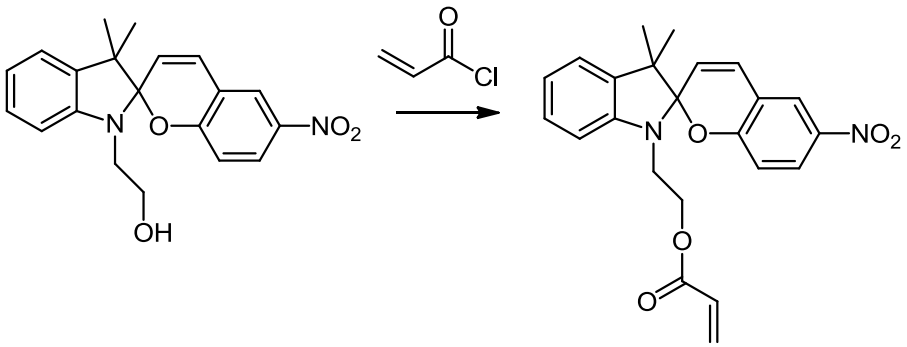

Figure 4.4 : Synthesis route of VSP

The FT-IR spectrum of SP in Figure 4.4 contains charactheristic pyran ring peak at 1651 cm^{-1}, -CH at 2962 cm^{-1}, -NO_2 at 1610 cm^{-1}, 1509 cm^{-1}, COC=C at 1479 cm^{-1}, 1333 cm^{-1}, 1273 cm^{-1}, 1022 cm^{-1}, C=O at 1720 cm^{-1}, CH=CH_2 at 1637 cm^{-1}.

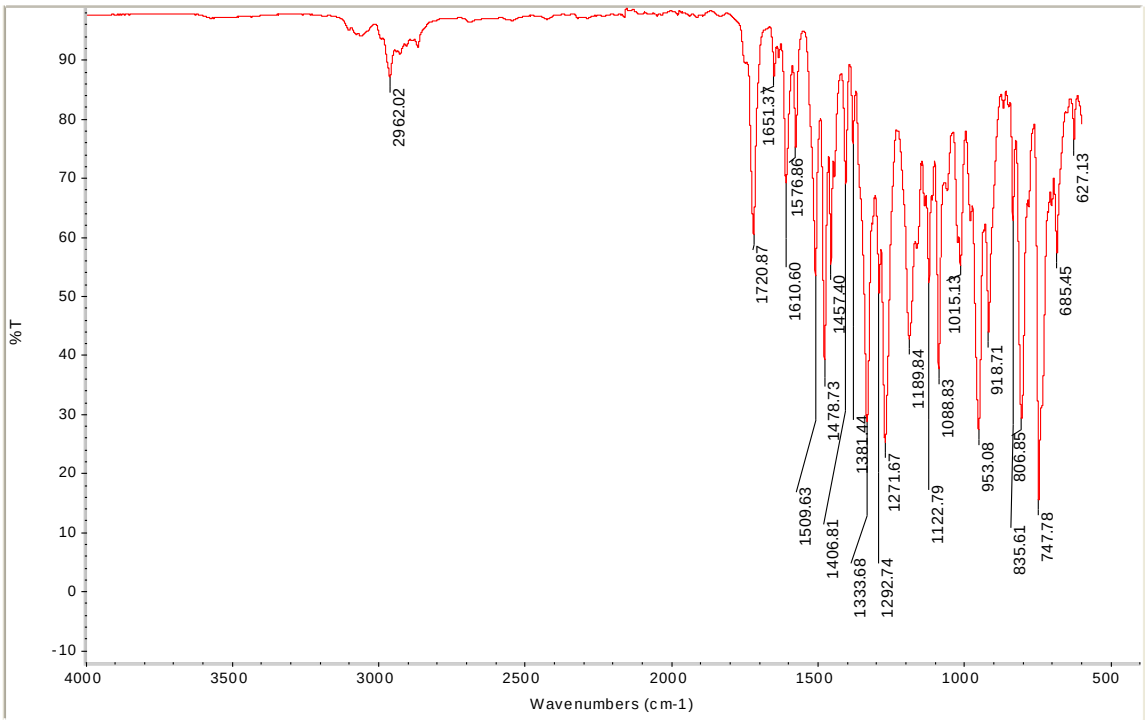

Figure 4.5 : FT-IR Spectra of VSP

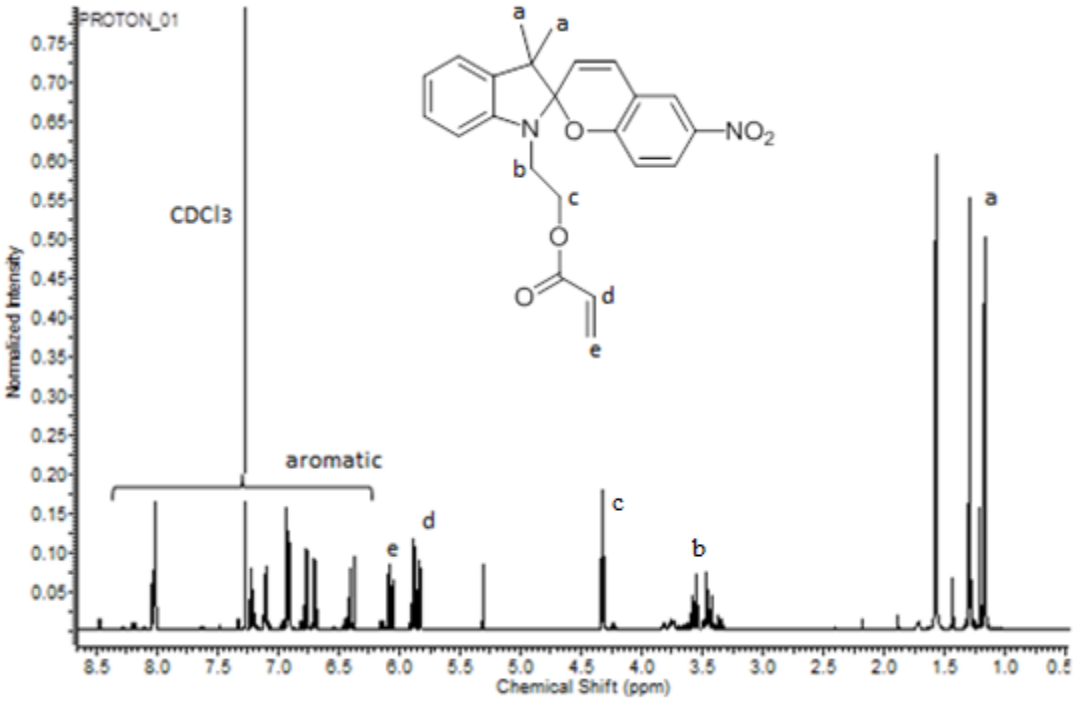

Figure 4.6 : ^{1}H NMR Spectra of VSP

4.2.1 Synthesis of spiropyran bearing urethane acrylate (SP-UA)

It was synthesized according to procedure mentioned in section 3.3.3 in Figure 4.7.

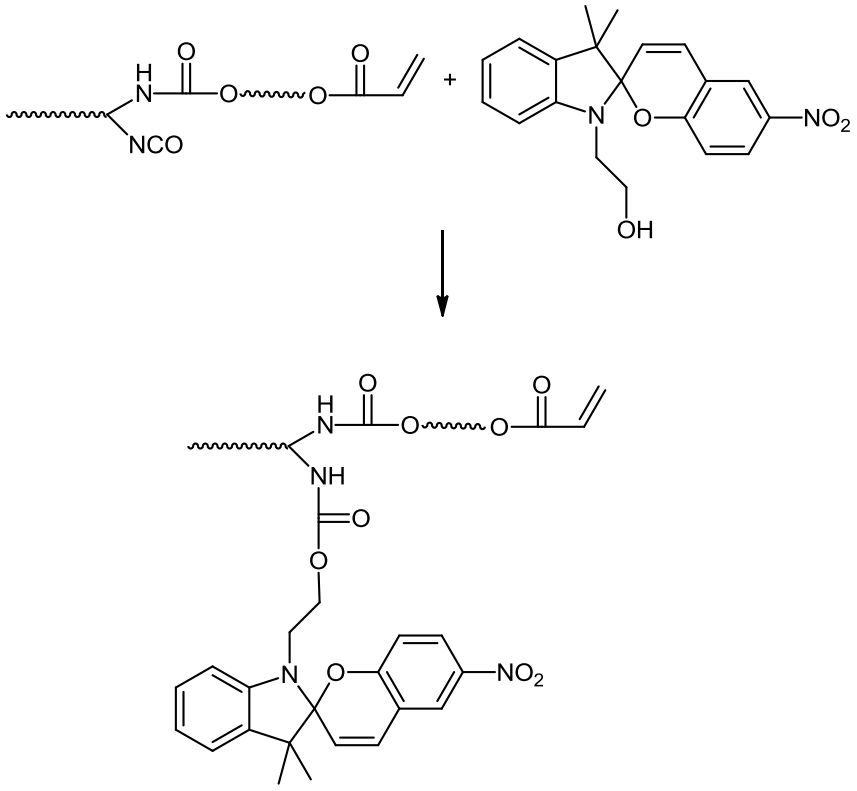

Figure 4.7 : Synthesis route of SP-UA

The IR spectrum in Figure 4.8 contains characteristic peaks of N-H (3338 cm^{-1}), and C=O (1714 cm^{-1}), -C-N- stretching bands (1577 cm^{-1}), C-H aliphatic stretching band (2933 cm^{-1}) are also observed. The disappearance of the absorption bands of the NCO group (2270 cm^{-1}) of NCO bearing urethane acrylate, which exists before reaction, also proves the synthesis of the urethane acrylate. Also the peaks appeared at 1610 cm^{-1}, 1335 cm^{-1},1269 cm^{-1} prove that SP was linked to urethane acrylate.

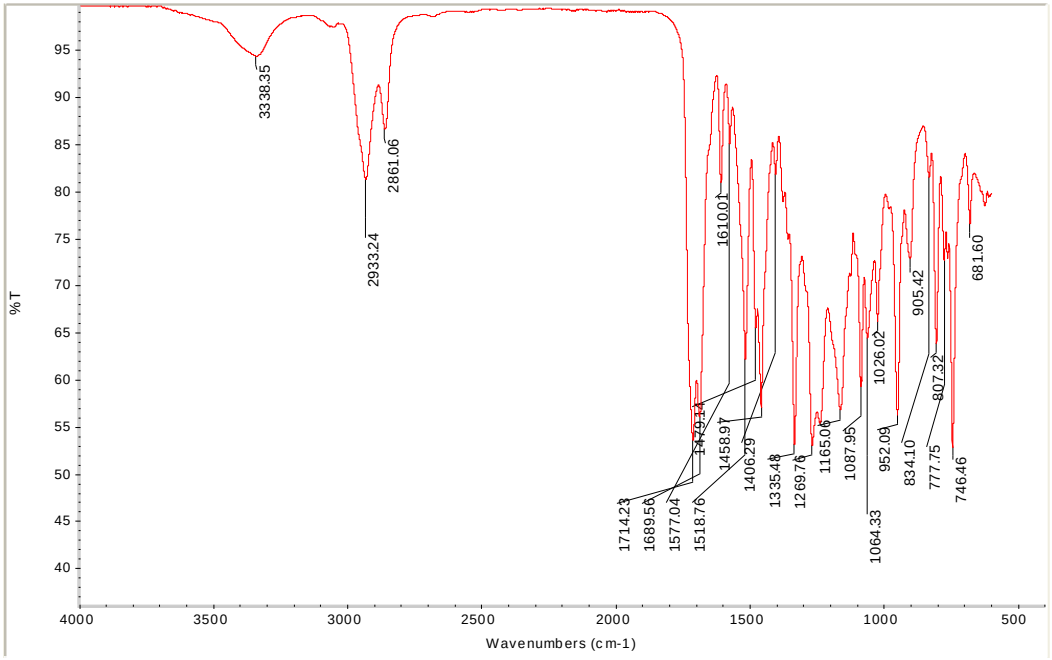

Figure 4.8 : FT-IR Spectra of SP-UA

4.2.2 Synthesis of spiropyran end fuctionalized poly(methyl methacrylate) via ATRP

Synthesis of polymer was shown in Figure 4.9.

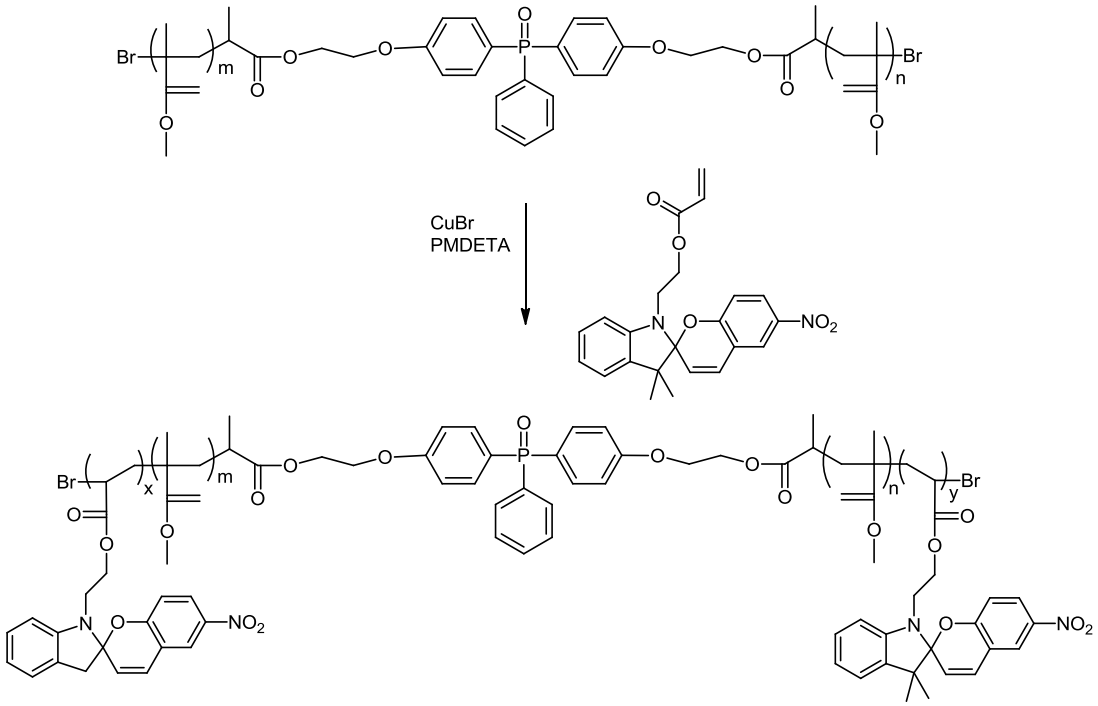

Figure 4.9 : Synthesis of spiropyran end functionalized PMMA

Table 4.1 : ATRP results.

Polymer	Mn	PDI
PMMA	9837	1.7
VSP-PMMA	12856	1.5

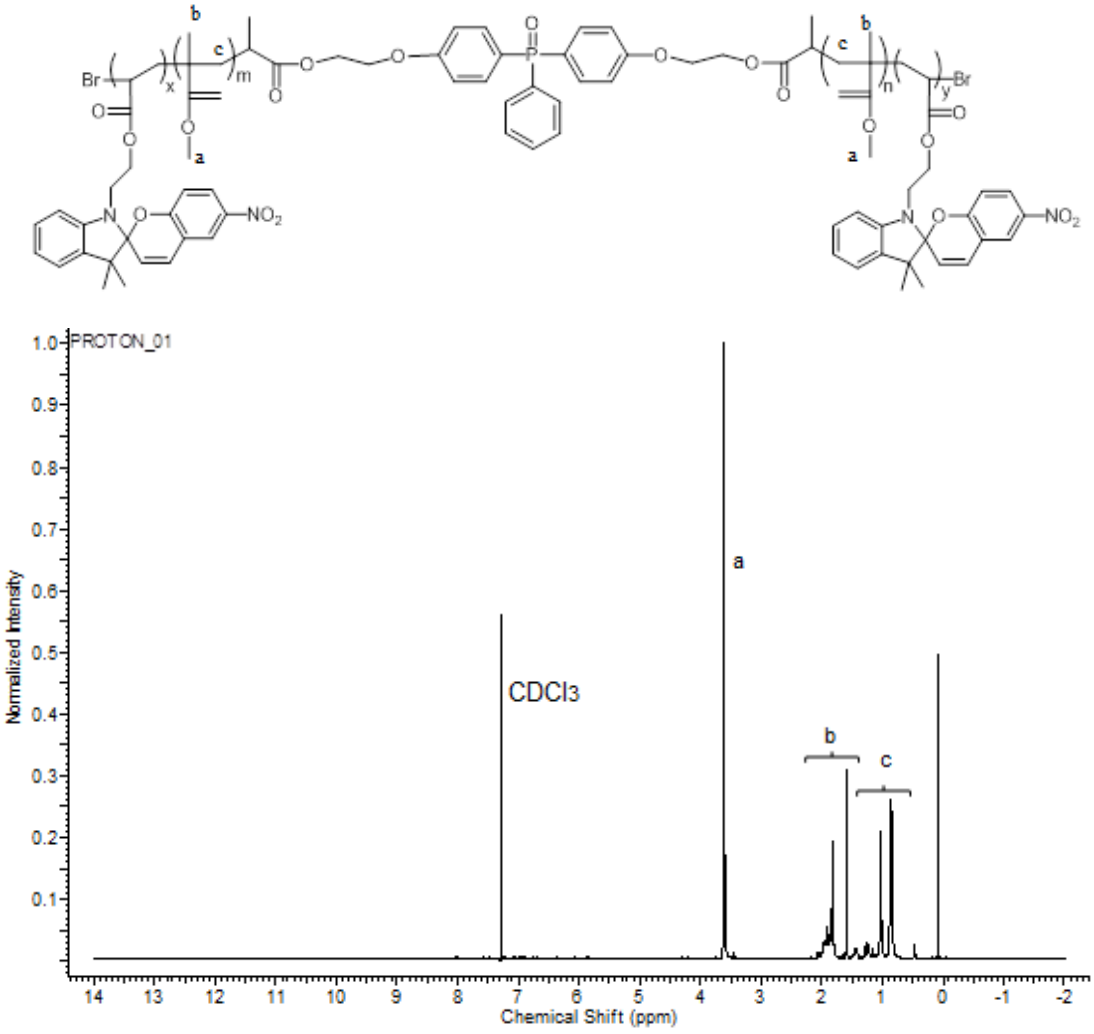

Figure 4.10 : ^{1}H NMR Spectrum of VSP-PMMA

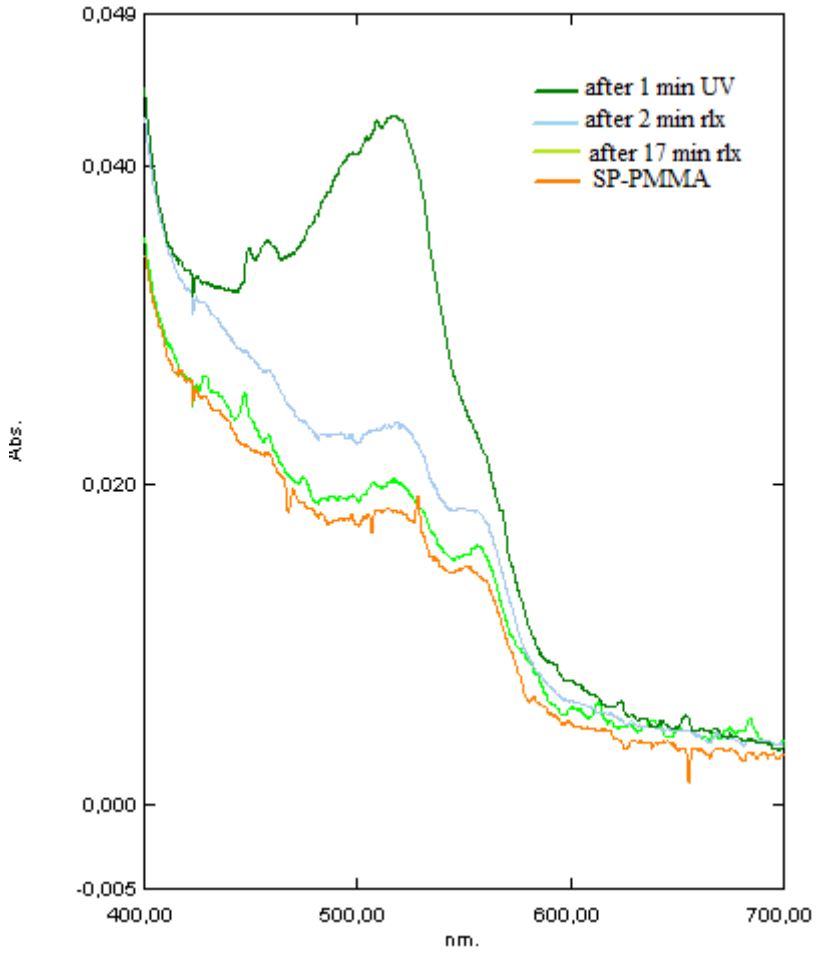

Figure 4.11 : UV absorption of SP-PMMA

From Table 4.1, molecular weight of SP-PMMA is compared with the macroinitiator, about seven SP groups were linked to PMMA end. For this reason, SP groups were not observed clearly in ^{1}H NMR spectra.

1 mg SP-PMMA was dissolved in 5 mL DCM and UV absorbance was measured in colorless form and after irradiation with UV for 1 min. Then, relaxation was measured after 2 min and 75 min. 75 min relaxation after 1 min irradiation SP-PMMA turned back colorless form.

4.3 Film Formation

Films were prepared according to procedure mentioned in section 3.4. Free films and coated plexiglasses were obtained by UV curing. In addition, samples were tested by methods mentioned in section 3.5.

4.3.1 UV spectroscopy analysis

UV spectroscopy was used to measure relaxation of films after UV curing process. According to photochromic compound, phthalocyanine containing and non containing films were compared among themselves.

All samples were kept in dark for 24 h for relaxation after UV curing process. Then, UV absorbance of films measured.

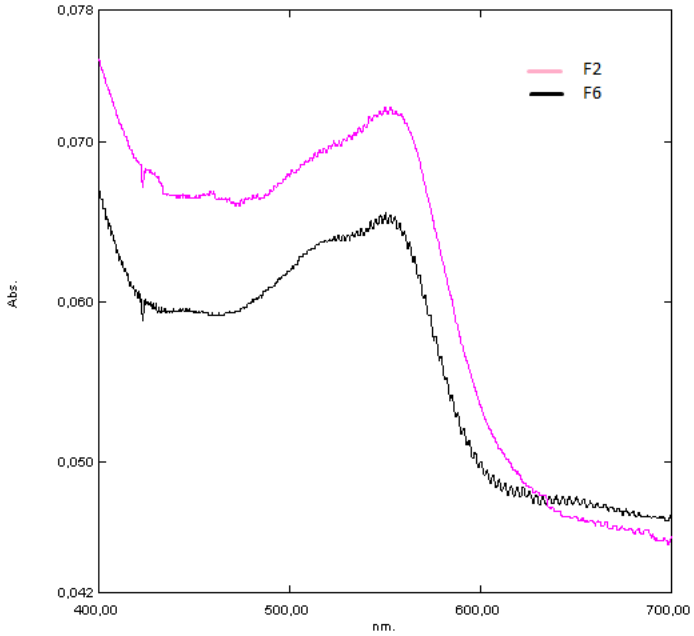

Figure 4.12 : UV absorption of VSP and VSP-F containing film

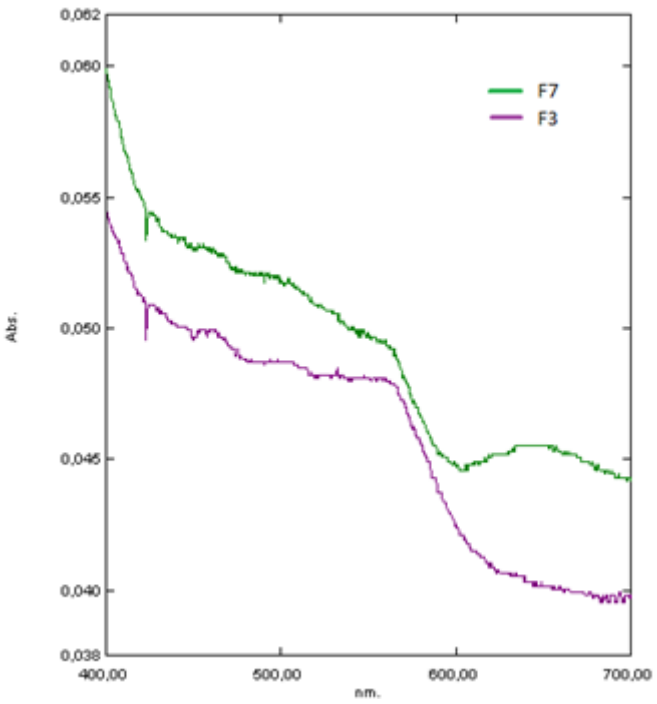

Figure 4.13 : UV absorption of SP-UA and SP-UA-F containing film

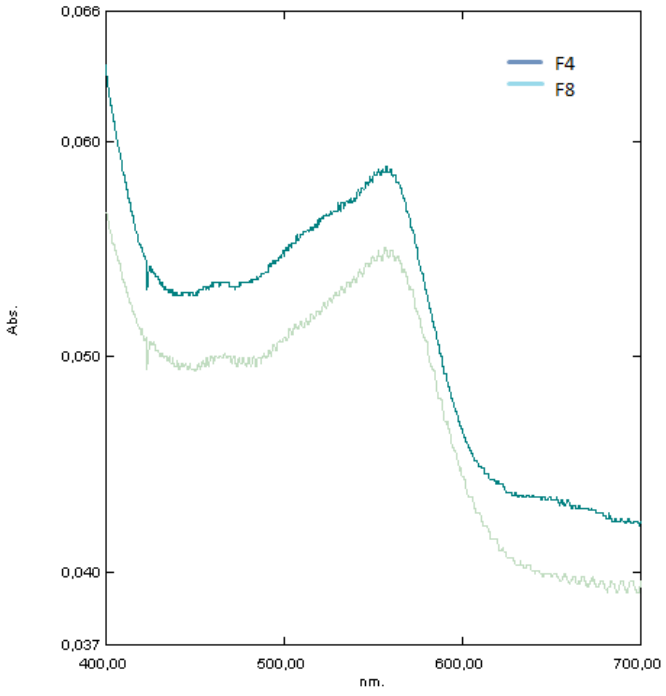

Figure 4.14 : UV absorption of SP and SP-F containing film

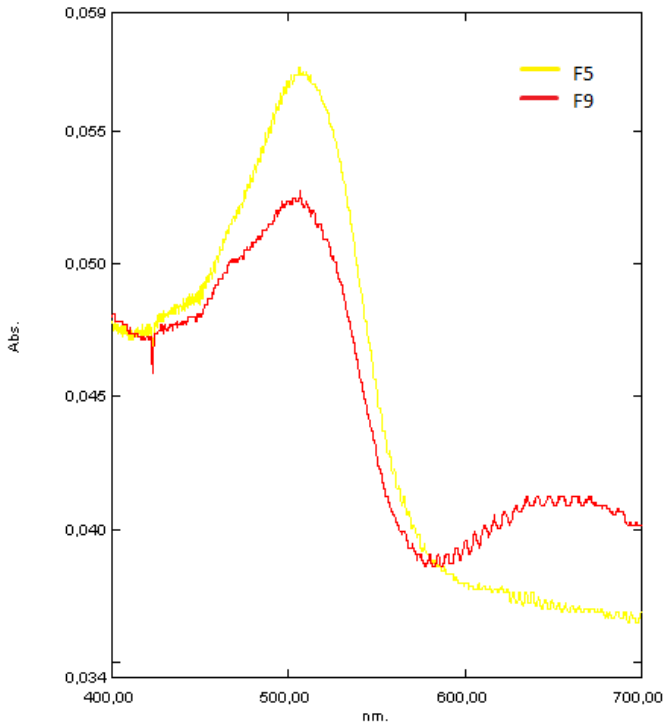

Figure 4.15 : UV absorption of SO and SO-F containing film

The samples containing phthalocyanine showed more faster ring-closing relaxation. It can be assumed that phthalocyanine accelerates reversion from open form to close form of photochromic compounds.

4.3.2 Gel content measuremet

This test was applied to measure the polymerization degree of the system. This procedure was proceeded as mentioned in section 3.5.3 and gel content values are listed in Table 4.2.

Table 4.2 : Gel content of cured films.

Sample Code	Gel Content (wt.)
F1	97
F2	97
F3	98
F4	96
F5	97
F6	97
F7	98
F8	96
F9	97

This results show us that unreacted part of cured materials are mostly under wt. 4%. It may be attributed that gel content values of the films increase because of high polymerization degree or crosslinking degree**.**

4.3.3 Contact angle measurement

The contact angle value of a liquid on a film is a direct reflection of the surface wettability. Contact angles of water were measured on plexiglass plates coated with four different urethane acrylate films. For each measurement one drop of water was tested on the surfaces and results are shown in Table 4.3.

According to results, spiropyran containing films (F2, F3, F4) more hydrophilic then blank (F1) because after UV curing spiropyran was switched to MC form which has hydrophilic character.

Phthalocyanine has hydrophobic character and it accelerates MC-SP transition SP also hydrophobic character. Therefore, spiropyran and phthalocyanine containing films (F6, F7, F8) were more hydrophobic then blank.

Spirooxazine has hydrophobic character, F5 was more hydrophobic than blank and phthalocyanine and SO containing film had the highest water contact angle since SO transition between open and closed form is rapid than SP.

Table 4.3 : Contact angle test results.

Sample Code	Water Contact Angle (^{o})
F1	64
F2	63
F3	61
F4	63
F5	78
F6	67
F7	78
F8	72
F9	83

4.3.4 Pendulum hardness test

König pendulum hardness test is applied after all formulations coated plexiglass plates.

Table 4.4 : Pendulum Hardness results.

Sample Code	Pendulum Hardness
F1	60
F2	57
F3	65
F4	56
F5	62
F6	56
F7	57
F8	61
F9	67

4.3.5 Pencil hardness

This test is applied to understand hardness of the surface in addition to pendulum hardness.

According to Table 4.5 SP containing films have good surface hardness, addition of phthalocyanine decreases the samples' surface hardness. SP containing films have more surface hardness than SO containing films.

Table 4.5 : Pencil Hardness results.

Sample Code	Pencil Hardness
F1	>7H
F2	>7H
F3	>7H
F4	>7H
F5	>3H
F6	>5H
F7	>4H
F8	>3H
F9	>6H

4.3.6 Tensile test

The mechanical specification of free films, prepared at 50x10x1mm dimensions, made clearly with measurement of stress-strain values. Stress-strain values for film formulations are given in Table 4.6.

Table 4.6 : Tensile test results.

Sample Code	Modulus (N/mm^2)	Tensile Strength (MPa)	Elongation at Break (%)
F1	331	17	11
F2	201	4	30
F3	217	23	41
F4	244	17	23
F5	288	18	26
F6	247	15	17
F7	238	17	24
F8	278	13	29
F9	299	9	20

According to Table 4.6 all samples are less stiff and more elastic than blank (F1).

Blank has the highest modulus, addition of photochromic compound decreases the modulus. Phthalocyanine has positive effect on modulus due to its aromatic structure.

The photochromic compound used in F3 was spiropyran linked urethane acrylate, F3 is more elastic than others. Also it has higher tensile strength.

Phthalocyanine containing films are more stiff and less elastic than just containing photochromic compound.

5. CONCLUSIONS

The aim of this work was synthesized photochromic coating materials. For this reason spiropyran based photochromic compounds were synthesized and used for UV curable urethane acrylate coatings.

The time constant for colorless spiropyrans to darken to the merocyanine reaction is very much slower. This study aimed to to increase the reaction rate for the reverse bleaching reaction with phthalocyanine. UV absorbance of cured films showed phthalocyanine effect on bleaching clearly.

Using VSP (F2) and SP-UA (F3) had negative effect on modulus but they increased elongation. SP (F4) has no acrylic group, that's why the modulus of this film was near to blank (F1) and elongation was greater than F1. SO (F5) had same affect like SP.

Synthesized photochromic groups made film more flexible.

Phthalocyanine addition increased modulus and decreased elongation.

Contact angle measurement of cured films showed the phthalocyanine effect of bleaching because phthalocyanine containing films had greater water contact angle than others.

Photoresponsive properties were observed successfully.

Gel content value of cured films varied from 96% and 98%.

Triphenyl phosphine oxide PMMA was used as bifunctional macroinitiator and VSP was added its end successfully via ATRP. UV absorbance of SP-PMMA was taken. From the GPC result, moleculer weight of polymer was increased from 9837 g/mol to 12856 g/mol and polydispersity index was decreased from 1.7 to 1.5.

REFERENCES

[1] **Luo, Q., Liu, Y., Tian H.** (2010). Photochromic Dithienylethene-Phthalocyanines and Their Analogs. In D. M. P. Mingos (Ed.), *Functional Phthalocyanine Molecular Materials*, 89-102. doi:10.1007/978-3-642-04752-76 c

[2] **Ramachadran, D., Urban, M. W.** (2011). Photochromic Responses in Polymer Matrices. In M. W. Urban (Ed.), *Handbook of Stimuli-Responsive Materials*, 223-240. doi:10.1002/9783527633739.ch9.

[3] **Kim, J., Kim, H., Han, J.** (2010). UV Curable Photochromic Composition and Products Formed by Using the Same. *United States Patent*. No: 2010/0213422 A1 dated 26.8.2010

[4] **Bamfield, P.** (2010). Phenomena Involving a Reversible Colour Change. *Chromic Phenomena: Technological Applications of Colour Chemistry*, 7-10. doi: 10.1039/9781849731034-FP001

[5] **Lu, S. Y., Hammerton I.** (2002). Recent developments in the chemistry of halogen-free flame retardant polymers. *Prog. Polym. Sci*., **27**, 1661-1712.

[6] **Ventura, C., Byrne, R., Audouin, F., Heise, A.** (2011). Atom transfer radical polymerization synthesis and photoresponsice solution behavior of spiropyran end-functionalized polymer as simplistic molecular probes. *Journal of Polymer Science Part A: Polymer Chemistry*, **49**, 3455-3463.

[7] **Laurent-Bouas, H., Dürr, H.** (2001). Organic photochromism. *Pure Appl. Chem.*, **73**, 4, 639–665.

[8] **Uchida, M., Irie, M.** (1993). Two-photon photochromism of a naphthopyran derivative. *J. Am. Chem. So.*, **115**, 6442-6443.

[9] **Parthenopoulos, D. A., Rentzepis, P. M.** (1989). Three-Dimensional Optical Storage Memory. *Science,* **245**, 843-845.

[10] **Atsuski, K., Atsuhiro, T., Takeru, H., Toyoji, O., Jiro, A.** (2010). Fast photochromic polymers carriying [2.2] paracyclophane-bridged imidazole dimer. *Macromolecules*. **43**, 3764-3769.

[11] **Minkin, V. I.** (2004). Photo-, thermo-, solvato-, and electrochromic spiroheterocyclic compounds. *Chem. Rev.*, **104**, 2751-2776.

[12] **Fissi, A., Pieroni, O., Angelini, L., Lenci, F.** (1999). Photoresponsive polypeptides. Photochromic and conformational behavior of spiropyran-containing poly(l-glutamate)s under acidconditions. *Macromolecules*, **32**, 7116-7121.

[13] **Kellman, A., Tfibel, F., Pottier, E., Guglielmetti, R., Samat, A., Razjmann, M.** (1993). Effect of nitro substituents on the photochromism of some spiro[indoline-naphthopyrans] under laser excitation. *J. Photochem. Photobiol. A*, **76**, 77-82.

[14] **Guo, X. et al.** (2004). 7-trifluoromethylquinoline-functionalized luminescent photochromic spiropyran with the stable merocyanine species both in solution and in the solid state. *J. Org. Chem.*, **69**, 8924-8931.

[15] **Wojtyk, J. T. C., Buncel, E., Kazmaier, P. M.** (1998). Effects of metal ion complexation on the spiropyran-merocyanine interconversion: development of a thermally stable photo-switch. *Chem. Commun.*, 1703-1704.

[16] **Prypsztejn, H. E., Negri, R. M.** (2001). An Experiment on Photochromism and Kinetics for the Undergraduate Laboratory. *J. Chem. Ed.*, **78**, 645-648.

[17] **Wojtyk, J. T. C. , Wasey, A., X Kazmaier, J. T. C., Hoz, S., Buncel, E.** (2000). Thermal Reversion Mechanism of N-Functionalized Merocyanines to Spiropyrans: A Solvatochromic, Solvatokinetic, and Semiempirical Study. *Journal of Physical Chemistry A*, **104**, 9046-9055.

[18] **Chibisov, A. K., Görner, J.** (1997). Photoprocesses in Spiropyran-Derived Merocyanines. *Journal of Physical Chemistry A*, **101**, 4305-4312.

[19] **Crano, J. C., Welch, C. N., VanGemert, B., Knowles, D., Anderson B**. (1993). Photochromic organic compounds in polymer matrices, *Photochemistry and Polymeric Systems*, 179–193.

[20] **Zahavy, E, Rubin, S., Willner, L.** (1994). Conformational dynamics associated with photoswitchable binding of spiropyran-modified concanavalin A. *Molecular Crystals and Liquid Crystals Science and Technology*, **246**, 195–199.

[21] **Miyashita, A., Hirano, M., Nakano, S., Nohira, H.** (1993). Diode-laser susceptible photochromic polymers: synthesis and photochemical properties of poly(methy1 methacylate) with spirobenzothiopyrans as side-groups. *Journal of Materials Chemistry*, **3**, 22l–222.

[22] **Ichimura, K.** (1994). Photoregulation of liquid crystal alignment induced by polarization photochromism of molecular films. *Molecular Crystals and Liquid Crystals Science and Technology*, **246**, 331–338.

[23] **Dvornikov, A. S., Rentzepis**, **P. M.** (1994). Photochromism: Nonlinear picosecond kinetics and 3D computer memory. *Molecular Crystals and Liquid Crystals Science and Technology*, **246**, 379–388.

[24] **Weiss, V., Friesem, A. A., Krongauz, V. A.** (1993). Holographic recording and all optical modulation in photochromic polymers. *Optics Letters*, **18**, 1089–l091

[25] **Chen, G. Q, Wu, Z. Q., Wu, J. R., Li, Z. C., Li, F. M.** (2000) Synthesis of alternating copolymers of N-substituted maleimides with styrene via atom transfer radical polymerization. *Macromolecules*, **33**, 232-234.

[26] **Curan, D. P.** (1988). The design and application of free radical chain reactions in organic synthesis. *Synthesis*, **7**, 489-568.

[27] **Patten, T. E., Matyjaszewski, K.** (1988). Atom transfer radical polymerization synthesis of polymeric materials. *Advanced Materials,* **10**, 901-915.

[28] **Wang, J. S., Matyjaszewski, K.** (1995). Controlled/"living" radical polymerization. atom transfer radical polymerization in the presence of transition-metal complexes. *Journal of the American Chemical Society*, **117**, 5614-5615.

[29] **Matyjaszewski, K., Wang, J. S**. (1998). WO 9630421, *US Patent,* **5**, 763,548.

[30] **Matyjaszewski, K., Xia, J.** (2001). Atom transfer radical polymerization. *Chemical Reviews,* **101**, 2921-2990.

[31] **Matyjaszewski, K., Davis, P.** (2002). *Handbook of radical polymerization.* Wiley-Interscience, New York.

[32] **McConnell, J.A., Willard, F.K.** (1990) Structure-Performance Relationships of Urethane Acrylates, Radiation Curing of Polymeric Materials, *ACS Symposium Series*, 272-283. Washington D.C. 28.12.1990.

[32] **Garcia, J. et al.** (1998). Phthalocyanines and Related Compounds: Subunits for the Preparation of Molecular Materials. *Tr. J. of Chemistry*, **22**, 23-31.

[33**] Lezno, C.C., Lever**, **A.B.P.** (1989). Phthalocyanines, Properties and Applications. Vol.1, VCH Publishers Inc., Cambridge.

[34] **Sakamoto, K., Ohno-Okumura, E.** (2009). Syntheses and Functional Properties of Phthalocyanines. *Materials, 2*, 1127-1179.

[35] **Hagena, J. P., Becerraa, I, Drakulicha, D., Dillonb, R.O.** (2001). Effect of antenna porphyrins and phthalocyanines on the photochromism of benzospiropyrans in poly(methyl methacrylate) films. *Thin Solid Films*, **398 –399**, 104–109.

[36] **Schwalm, R.** (2007). *UV coatings*, The Netherlands.

[37] **Mehnert, R., Pincus, A., Janorsky, I., Stowe, R., Berejka, A.** (1998). *UV&EB Curing Technology & Equipment*, John Wiley & Sons Ltd./ Chichester and SITA Technology Ltd., London, p. 1

[38] **Schwalm., R.** (2006). *UV Coatings, Basic, Recent Developments and New Applications*, Elsevier Science.

[39]**Crivello, J.V. and Ahn, J.** (2003). Synthesis and characterization of second-generation S,S-dialkyl-S-(dimethylhydroxyphenyl)sulfonium salt photoinitiators. *J. Polym. Sci. Polym. Chem. Ed*., **41**, 2556–2569.

[40] **Dietliker, K. and Crivello, J.V.** (2000). *Photoinitiators for free radical, cationic and anionic photopolymerization* (2nd ed.) (Vol. 3.) New York, NY: Wiley.

[41] **Bradley, G.** (1998). In Chemistry and Technology of UV and EB Formulation for Coatings, *Inks and Paints*. John Wiley and Sons/SITA Technology.

[42] **Allen, N. (Ed.)** (1989). *Photopolymerization and photoimaging science and technology*. Springer Netherlands, 40–44.

[43] **Raymo, F. M., Williams, D. J.** (2003). Digital processing with a three-state molecular switch. *J. Org. Chem.*, **68**, 4158-4169.

[44]**Wang, S., Chunyang, Y., Choi, M. S., Kim, S. H.** (2007). Synthesis and switching properties of photochromic carbazole-spironaphthoxazine copolymer. *J. of Photochem. and photobiol. A: Chemistry*, **192**, 17-22.

[45] **Turel, B., Karatas, S., Gungor, A., Serhatlı, I. E.** (2012). Synthesis of Triphenyl Phosphine Oxide-Containing Polymers via Atom Transfer Radical Polymerization. *J. Appl. Polym. Sci*., **128**, 888-898.

[46] **Ramachandran, V. S., Beaudoin, J. J.** (2001). *Handbook of analytical Techniques in Concrete Science and Technology*. New York, William Andrew Publishing.

[47] **Lam, C. N., Wu, R., Li, D., Hair M. L., Neumanna**, **A. W.** (2002). Study of the advancing and receding contact angles: liquid sorption as a cause of contact angle hysteresis. *Adv Colloid Interface Sci.*, **96**, 169-191.

[48] **Koleske, J.V. (**1995). *Paint and coating testing manual* (4th ed.) Philadelphia, Astm Intl.

[49] Paints and Varnishes: Pendulum damping test, ISO 1522:2006, third ed.

[50] **Pilkey, W. D.** (2005). *Formulas for stress, strain, and structural matrices*. (2nd ed.). Hoboken, NJ : Wiley.

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